

DETERMINATION OF TOXIC HEAVY METALS IN WET
DEPOSITION AND AMBIENT AIR IN COLUMBUS,
GEORGIA

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**DETERMINATION OF TOXIC HEAVY METALS IN WET
DEPOSITION AND AMBIENT AIR IN COLUMBUS,
GEORGIA**

A Thesis in

Environmental Science

by

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*Submitted in Partial Fulfillment
of the Requirements
for the Degree of*

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*Dedicated to my parents Gilbert and Kathleen Nestor
and my brothers Matthew and Lindbert for their support,
encouragement and inspiration*

I have submitted this thesis in partial fulfillment of the requirements for the degree of Master of Science

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Table of Contents

Abstract.....	vi
List of Figures.....	viii
List of Tables.....	x
List of Acronyms and Abbreviations.....	xi
Acknowledgements.....	xiii
Chapter 1. Introduction.....	1
1.1. Purpose of study.....	2
1.2. Pollution sources.....	3
1.2.1. Natural sources.....	3
1.2.2. Anthropogenic sources.....	3
1.3. Uses of heavy metals.....	4
1.4. Movement of heavy metals in the environment.....	4
1.4.1. Heavy metals in the air.....	5
1.4.2. Atmospheric deposition.....	8
1.4.2.1. Dry deposition.....	8
1.4.2.2. Wet deposition.....	8
1.5. Heavy metals in the aquatic environment.....	9
1.6. Heavy metals in soils and vegetation.....	10
1.7. Essential and non-essential heavy metals.....	10
1.7.1. Heavy metal toxicity.....	11
1.7.1.1. Lead (Pb).....	11
1.7.1.2. Arsenic (As).....	12
1.7.1.3. Cadmium (Cd).....	14
1.7.1.4. Chromium (Cr).....	15
1.8. Air quality in Georgia.....	16
1.8.1. Description of study area.....	17
1.8.2. Climatology.....	18
Chapter 2. Methodology.....	22
2.1. Sampling site selection.....	22
2.2. Sampling.....	23
2.2.1. Ambient air samples.....	23
2.2.2. Wet deposition samples.....	23
2.3. Sample pretreatment.....	23
2.4. Reagents and Standards.....	24
2.5. Instrumentation.....	24
2.6. Calibration.....	25
2.7. Determination of Pb, Cr, As and Cd using GF-AAS.....	25
Chapter 3. Results and Discussion.....	28
3.1. Optimization of ashing and atomization temperatures.....	28
3.2. Limits of detection (LOD).....	29
3.3. Validation of the analytical procedures.....	30

3.4. Analysis of wet deposition samples.....	31
3.4.1. Heavy metal concentration trends in wet deposition	31
3.4.2. Monthly variation of heavy metals in wet deposition.....	39
3.4.3. Seasonal variation of heavy metals in wet deposition	41
3.5. Correlation between heavy metals in wet deposition	42
3.6. Correlation between heavy metals and amount of precipitation.....	44
3.7. Analysis of ambient air samples	45
3.7.1. Heavy metal concentration trends in ambient air	45
3.7.2. Monthly concentrations of heavy metals in ambient air.....	52
3.7.3. Seasonal variation of heavy metals in ambient air.....	54
3.8. Correlation between heavy metals in ambient air.....	56
3.9. Comparison between wet deposition and ambient air	57
Conclusion and Future Work.....	57
Conclusion	58
Future work.....	60
References.....	61

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ABSTRACT

Atmospheric pollution is one of the most significant and potentially catastrophic environmental issues threatening the United States and the world today. One such source of this pollution is heavy metals. The impact of heavy metal pollution on living organisms can be disastrous, having the potential to cause the deterioration of ecosystems and posing danger to the health and survival of the human race. Chronic and acute human exposure to this type of pollution can damage the proper functioning of vital body organs by inhibiting important neurological pathways. In plants, it essentially acts as a counter-agent to proper growth. In areas across the United States and the World, anthropogenic sources have been a large contributing factor to the exacerbation of heavy metal concentrations in the atmosphere. Certain particulate matter and even some common aerosols harbor toxic heavy metals like arsenic, lead, chromium and cadmium and are thus categorized as 'hazardous air pollutants' by the U.S. EPA. The heavy metal pollutants that exist suspended in the air are subject to wet and dry atmospheric deposition. From the air they may be released by precipitation events or direct dry deposition unto various environmental compartments near or far from their sources. These have caused increased concern since they are known to persist in the environment. In this study, wet deposition and ambient air samples were collected over a 15 month period at a single site on Columbus State University's main campus in Columbus, Georgia, United States. The concentrations of lead, cadmium, chromium and arsenic in ambient air and wet deposition samples were determined using Atomic Absorption Spectroscopy. A comparison between concentrations of heavy metals in ambient air and concentrations in wet deposition are presented. The monthly and seasonal variations of lead, cadmium, chromium and arsenic are examined. A comparison between concentrations for individual heavy metals, in dry and wet deposition was also conducted. The concentrations of Cd, Cr, Pb and As in wet

deposition samples ranged from ND to 0.656 $\mu\text{g/l}$, ND to 20 $\mu\text{g/l}$, ND to 0.8 $\mu\text{g/l}$ and 0.103 $\mu\text{g/l}$ to 10.5 $\mu\text{g/l}$, respectively. Concentrations of Cd, Cr, As and Pb in ambient air samples ranged from 0.679 ng/m^3 to 17.36 ng/m^3 , ND to 116 ng/m^3 , ND to 32.80 ng/m^3 and 1.78 ng/m^3 to 33.30 ng/m^3 , respectively. Cd and Pb showed high monthly and seasonal variability in ambient air samples. In addition, a strong correlation was observed between Cd and Pb in ambient air indicating that they may have originated from the same source. Overall, results imply that traffic emissions and construction are the most likely sources for heavy metals in this study.

Key words: Heavy Metals, Atmospheric Deposition, Ambient Air, Graphite Furnace Atomic Absorption Spectroscopy, Pollution

LIST OF FIGURES

Figure	Page
1. Routes and fate of heavy metals in environmental compartments	5
2. Transport and effects of air pollution in urban areas	6
3. Pollution source and corresponding particle size	7
4. Atmospheric deposition of pollutants	9
5. Sources of human exposure and modes of toxicity of arsenic.....	14
6. Air pollution monitoring sites in Georgia	16
7. Heavy metal monitoring sites in Georgia	17
8. Location of Columbus, Georgia in the United States.....	18
9a) Percent metal detection at air quality monitoring sites in Georgia from 2005-2009...	20
b) Percent metal detection and average concentration of metal species at monitoring sites from 2005-2009	20
10. Lead emissions in the state of Georgia in 2005	21
11. Ambient air and wet deposition sample collection site	22
12. GFA-7000 with flame and graphite furnace units	25
13. Atomic absorption theory	26
14. Atomic absorption spectroscopy.....	27
15. Concentration trends of heavy metals in wet deposition in Columbus, GA	
a) Cadmium	35
b) Chromium.....	36
c) Arsenic.....	37
d) Lead.....	38
16. Monthly concentrations of heavy metals in wet deposition samples	40
17. Seasonal variation of heavy metals in wet deposition samples	42
18. Correlation between heavy metals in wet deposition: a) Cr and Pb, b) Cd and Cr, c) Cd and Pb, d) Cd and As, e) Cr and As, and f) Pb and As..	43
19. Correlation between precipitation (mm) and heavy metal concentrations.	44
20. Concentration trends of heavy metals in ambient air.	47

a) Cadmium.....	48
b) Chromium.....	49
c) Arsenic.....	50
d) Lead.....	51
21. Monthly concentrations of heavy metals in ambient air samples.....	53
22. Seasonal variation of heavy metals in ambient air samples	55
23. Correlation between heavy metals in ambient air: a) Cr and Pb, b) Cd and Cr, c) Cd and Pb, d) Cd and As, e) Cr and As, and f) Pb and As	56

LIST OF TABLES

Table	Page
1. Percentage release of heavy metals from natural sources	3
2. Uses of some heavy metals.....	4
3. Concentration and health defects of lead in the blood.....	12
4. Toxic effects of cadmium exposure on human health	15
5. 2009 Climatology report for Columbus, Georgia.....	19
6. 2010-2011 Climatology report for Columbus, Georgia	19
7. Temperature programs.....	28
8. Limits of detection	30
9. Validation of the analytical procedures	30
10. Correlation between heavy metals in wet deposition and ambient air	57

LIST OF ACRONYMS AND ABBREVIATIONS

ACS	American Chemical Society
Ar	Argon
As	Arsenic
ATP	Adenosine Triphosphate
Ave	Average
Cd	Cadmium
Cr	Chromium
CSU	Columbus State University
Cu	Copper
DF	Degrees of Freedom
DNA	Deoxyribonucleic Acid
EPA	Environmental Protection Agency
GADNR	Georgia Department of Natural Resources
GEPD	Georgia Environmental Protection Department
GFAAS	Graphite Furnace Atomic Absorption Spectrophotometry
HCl	Hydrochloric Acid
HDPE	High density Polyethylene
Hg	Mercury
HNO₃	Nitric Acid
Km	Kilometers

LOD	Limits of Detection
MCL	Maximum Contamination Level
mm	Millimeter
Mn	Manganese
Mo	Molybdenum
MS	Mean Squared Deviation
ND	Not Detected
Ni	Nickle
OSHA	Occupational Safety and Health Administration
P	Alpha values; ($P < 0.05$) Statistically Significant
Pb	Lead
PEL	Permissible Exposure Limit
REC	Recreation
RSD	Relative Standard Deviation
Sb	Antimony
TSP	Total Suspended Particles
WD	Wet Deposition
WHO	World Health Organization
Zn	Zinc

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Chapter 1: Introduction

Atmospheric pollution is one of the most significant and potentially catastrophic environmental issues threatening the United States and the world today. As cities continue to expand, more and more pollutants are released into the atmosphere creating an increasingly hazardous environment for communities and their inhabitants. This constant degradation of the atmosphere is so considerable that it possesses the potential to eventually render the air unsuitable for breathing.

In 1999, the United States EPA reported that hazardous air pollutants emissions exceeded 10 million pounds or 4,535 923.7 kg (Salzman and Thompson, 2007). The significance of this report is seen in the potential of these pollutants to cause a range of health issues including cancer, neurological defects, respiratory defects, reproductive damage and other negative health conditions. The extent to which these pollutants affect human health depends on the type of pollutant and duration of exposure to the pollutant (Salzman and Thompson, 2007).

Metals of high atomic mass that cannot be processed by living organisms due to toxicity are commonly known as heavy metals (Duffus, 2001). These metals are generally found in a wide array of groups on the periodic table. Exposures to these types of toxic metals are a health hazard for humans (Cao *et al.*, 2009). In general, these heavy metals are non-biodegradable and are considered persistent contaminants of the environment (Duruibe *et al.*, 2007). They may also bioaccumulate up the food chain hence becoming a threat to living organisms.

Toxic heavy metals are one of the major hazardous pollutants that affect us today. Atmospheric deposition of toxic heavy metals has stimulated profound research all over the world due to the extent of their harmful effects on living organisms (Shrivastav, 2001). Toxic metals like lead (Pb), cadmium (Cd), arsenic (As) and chromium (Cr) can essentially attack specific areas in the human body upon exposure (Shinggu *et al.*, 2007). Their dispersion and transport in the atmospheric layers may be exacerbated by human activities and natural phenomenon. The resulting high concentrations of these metals in

the air may lead to both ecotoxic effects on plants and animal species, and toxic effects to humans.

Rapid urbanization and increases in the number of motor vehicles on roadways have heightened concentrations of heavy metals in the air above levels at which they naturally occur (Xiao-li *et al.*, 2006). Evidently, some of these metals are essential for life at very low concentration levels but at high levels of concentration they may lead to harmful effects in humans, plants and animals. Those that are of grave concern are the non-essential toxic heavy metals like As, Pb, Cd and Cr which may be considered major air and land pollutants in areas where they are most concentrated (Moses *et al.*, 2009).

In the air, heavy metals exist in combination with dusts from sediments and suspended breathable particles (Adriaenssens, 2007). From the air they may be released by precipitation events or direct dry deposition into various environmental compartments near or far from their sources. An intense study of the levels of heavy metals like Pb, Cd, Cr, and As in the atmosphere is therefore both necessary and vital to providing a safer environment and is imperative in securing man's general well being.

1.1. Purpose of study

This study was conducted in order to determine toxic heavy metals in ambient air and wet deposition in Columbus, Georgia, located in the south east region of the United States. This type of research will aid in assessing air pollution with respect to heavy metals in Columbus and inevitably provide invaluable information on possible sources that may influence population health in the future.

The five main objectives of this research were to:

- Determine the concentrations of lead, cadmium, arsenic and chromium in atmospheric wet deposition and ambient air samples.
- Compare monthly variations of heavy metals.
- Compare seasonal variations in the concentrations of heavy metals.
- Investigate the relationship between wet deposition and amount of precipitation.

- Compare heavy metal concentrations in wet deposition and ambient air samples.

1.2. Pollution sources

Toxic heavy metals are released into the environment from a variety of sources, both natural and anthropogenic.

1.2.1. Natural sources

Naturally occurring heavy metals may exist in the form of vapors, ions dissolved in water and as minerals or salts found in rock, soil and sand. According to Pacyna (Pacyna, 2002), biogenic sources account for more than half the Hg and Mo released into the atmosphere, and for 30% to 50% of the As, Cd, Cu, Mn, Pb and Zn released (Table 1). Soils may account for a significant amount of heavy metals release into the atmosphere.

Table 1. Percentage release of heavy metals from natural sources (Pacyna, 2002)

Natural Source	Percent Released into the Atmosphere
Biogenic	> 50% Hg, Mo 30-50% As, Cd, Cu, Mn, Pb and Zn
Volcanic Gas	40% to 50% of Cd and Hg 20% to 40% of the As, Cr, Cu, Ni, Pb, and Sb
Sea Aerosols	10% various heavy metals

1.2.2. Anthropogenic sources

Heavy metals are not only introduced to the environment by way of natural sources but also through human activities that cause constant dispersion in various environmental compartments. Waste incineration sites, runoff from agricultural land, traffic emissions and effluent from urban areas release heavy metals into the environment (Qishlaqi and Moore, 2007). Industrial sources may cause a major hazard especially in heavily populated areas. In addition, the combustion of fuels from stationary sources by means of both external combustion and internal combustion may be significant to the dispersion of heavy metals in the atmosphere.

1.3. Uses of heavy metals

The uses of heavy metals range from electrical materials to stainless-steel manufacturing (Table 2). Chromium for example, has been widely used in the production of steel, chrome plating, manufacture of dyes and pigments, leather and wood preservation treatments (U.S EPA, 2000). Other general uses of heavy metals include drilling muds, textiles, and in copying machine toners (ATSDR, 2010).

Table 2. Uses of some heavy metals (Hardy *et al.*, 2008)

Heavy Metal	Use
Cadmium	Components in manufacture of solder, electrical supplies, barriers to control nuclear fission, phosphors in the production televisions, anticorrosive coatings for metals, bearing alloys, amalgam in dentistry and worm treatments for swine and poultry. Cement production.
Arsenic	Component in manufacture of bronze materials, fireworks, shot, agricultural chemicals, laser materials, glass, semiconductor materials, wood preservatives, copper, and lead alloys and insecticides.
Nickel	Component of manufacture of stainless steel, other corrosion-resistant alloys, coins, nickel steel for armor plates, burglarproof vaults, vegetables oils, ceramics and greenish glass, Al-Ni-Co magnets and Ni-Cd batteries.
Lead	Component in manufacture of older paints, older plumbing hardware, ammunition, solder, metals, storage batteries, sound and vibration absorbers, lead gasoline, obsolete insecticides (lead arsenate), lead crystal and flint glass.
Chromium	Component of the manufacture of steel, stainless-steel, alloys, metal plating for prevention of corrosion, coloring agents for emerald green glass, chemical analysis, leather tanning, textile color pigments and mordants, and trace minerals essential to the nutrition of man and animals.
Copper	Component in metal alloys, electrical wiring, some water pipes, preservatives for wood, leather and fabrics and some agricultural fungicides.
Zinc	Widely used in industry to make dye, paint and rubber; wood preservatives and ointments.

1.4. Movement of heavy metals in the environment

The presence, movement and fate of heavy metals in various environmental compartments have become increasingly important to environmentalists. The nature of these metals has also gained central importance since it determines the extent to which plants and animals are affected. The movement of toxic heavy metals through the environment can be influenced by wind and other atmospheric eddies that assist their transport from one place to another.

(Kinnersley and Scott, 2001). When heavy metals are released from their source they may be introduced to terrestrial and aquatic environmental systems by precipitation (wet deposition) and through the direct release on land or water surfaces (dry deposition). Heavy metals that accumulate in natural rocks and sediments affect aquatic plants and animals whereas those released from the air may directly affect soils, terrestrial plants and animals and ultimately humans (Figure 1).

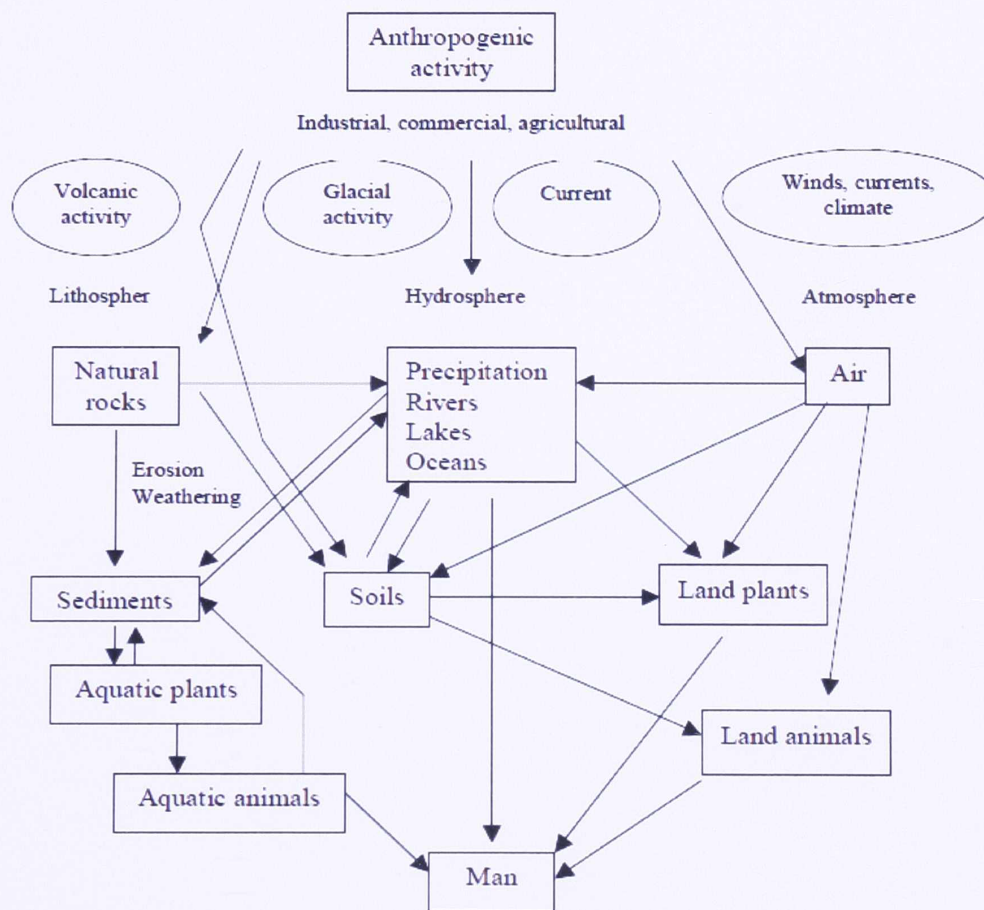


Figure 1. Routes and fate of heavy metals in environmental compartments (Abegaz, 2005)

1.4.1. Heavy metals in the air

The vertical extent of the atmosphere is thinner than the horizontal and as a result most of the motion that takes place in the atmosphere occurs horizontally rather than vertically (Jacob, 1999). The horizontal movement of particles in the air makes it easier for pollutants to reach surface water, soils and vegetation. Winds play a key role in this type

of movement. Influenced by climatic changes, winds may carry atmospheric pollutants far distances away from their source. When pollutants are emitted from their source, they are dispersed with the help of wind speed and direction, transformed through chemical reactions with other elements and distributed to the receiving environment (Figure 2). In this regard both aerosols and particulate matter are fundamentally important.

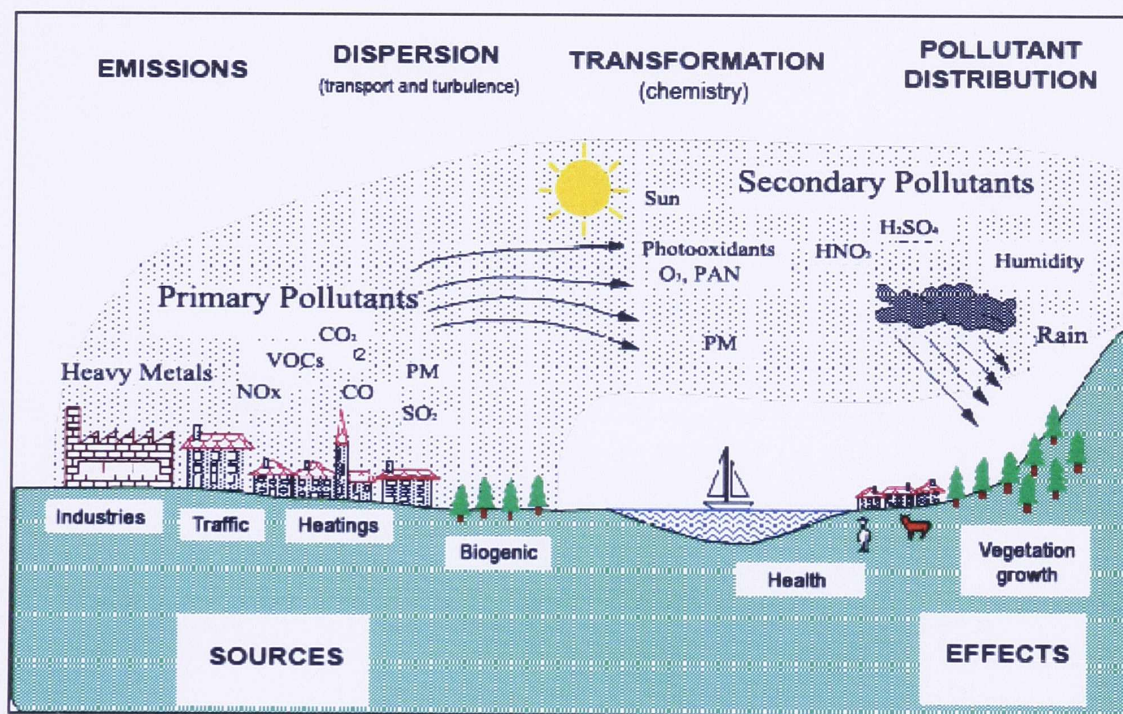


Figure 2. Transport and effects of air pollution in urban areas (Malakooti, 2010)

One of the major causes of air pollution in urban environments is atmospheric aerosols (Johnson *et al.*, 2006). Aerosols are various liquids and solids dispersed in different phases in the air (Raghava and Kalliat, 2009). They have the ability to form heterogeneous mixtures with major air pollutants hence affecting air quality (Johnson *et al.*, 2006). In the atmosphere, there are two main forms of aerosols. One phase includes solid or liquid particles and the other phase includes gases in which the solid and liquid particles are suspended. These aerosol particles may originate from both natural and anthropogenic sources in the environment.

Aerosols comprise a wide range of sizes and a wide variety of shapes. In 2007, the Intergovernmental Panel for Climate Change (IPCC) reported that aerosols originated

from a number of sources in the environment, one of which is known as mineral dust (IPCC, 2007). They concluded that these particles can make up a large portion of the process of particle loading in the atmosphere. The IPCC (IPCC, 2007) also identified sea salt as a major producer of aerosols. In urban environments, industrial dust and primary anthropogenic aerosols that originate from transportation, coal combustion, cement manufacturing, metallurgy and waste incineration are characteristic of the composition of urban aerosols (Raghava and Kalliat, 2009).

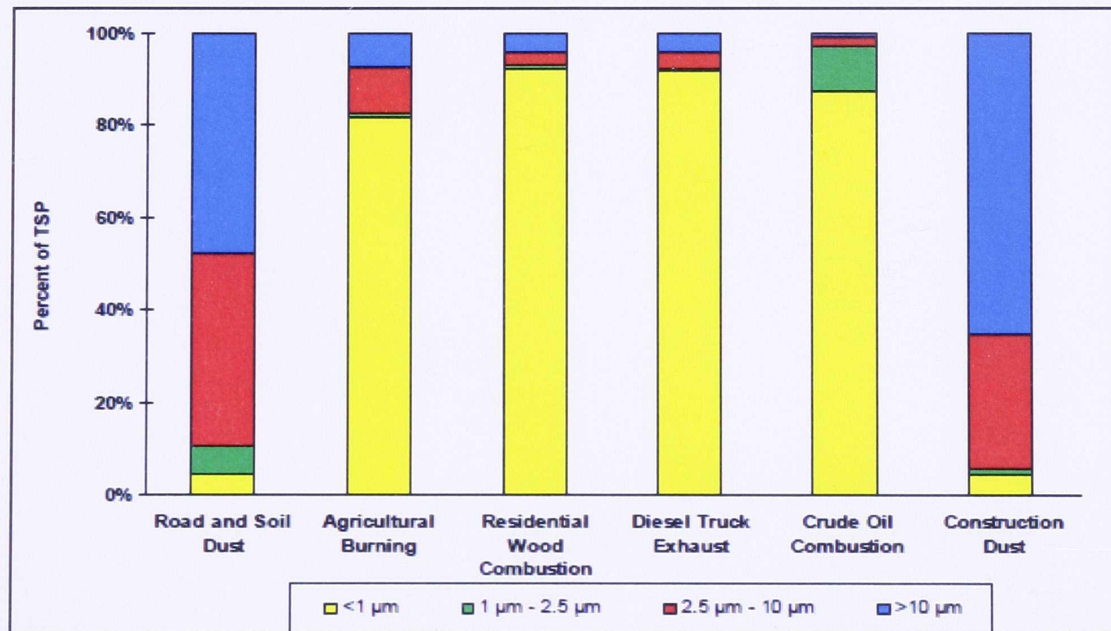


Figure 3. Pollution source and corresponding particle size (Pederson, 2006)

Particulate matter is critical to air pollution. Particulate matter comprises solid and liquid droplets (http, 1). As one of the six criteria air pollutants, it has the ability to cause harmful health effects to humans exposed to it (Fierro, 2000). According to the U.S. EPA, particulate matter is divided into two major categories. These categories include inhalable coarse particles that are larger than $2.5\mu\text{m}$ and smaller than $10\mu\text{m}$ (PM_{10}) and fine particles that are $2.5\mu\text{m}$ and smaller (http, 1). PM_{10} can be found in a variety of sources such as fire places, construction dust, motor vehicles and industrial activities (http 2). Fine particles such as $\text{PM}_{2.5}$ found in soil and road dust have been monitored all over North America and in Europe (Van Donkelaar *et al.*, 2010). Because they are so small they have the potential to cause tremendous adverse effects on human health. In

addition, studies have shown that PM₁₀ particles have caused cardiopulmonary morbidity and mortality (Van Eeden *et al.*, 2001). The sources of pollution and corresponding particle sizes are shown in Figure 3.

1.4.2. Atmospheric deposition

Dispersion of heavy metals by atmospheric deposition is a worldwide problem (Brus *et al.*, 2002). Deposition of toxic metals may not only affect humans but also vegetation. According to Jacob (Jacob, 1999), the concept of deposition means that all material in the atmosphere is deposited back on the surface of the earth. When atmospheric particles like aerosols and particulate matter are aggregated or washed out by precipitation the process is referred to as atmospheric deposition (Azimi *et al.*, 2003). This phenomenon of atmospheric deposition occurs in both wet and dry forms (Muezzinoglu and Cizmecioglu, 2006). The effects of both of these forms of heavy metal deposition on health may be seen in both rural and urban areas. Moreover, in areas where the climate is subtropical, both forms of deposition may be important when measuring atmospheric pollutants.

1.4.2.1. Dry deposition

In dry deposition, particles may be deposited directly unto land and water by gravitational force. Azimi (2005) explains that in the process of atmospheric deposition pollutants are partitioned between particulate liquid and vapor phases. This occurs as a result of the different physical and chemical properties, size and composition of the source particles. Emission of gases and other particles from the earth's surface significantly influence the processes involved in dry deposition by the dry-air particle exchange (Wesely and Hicks, 2000). This type of deposition is a driving force in toxic heavy metal loading into aquatic systems and the negative health effects on both terrestrial and aquatic environments (Han *et al.*, 2004; Yi *et al.*, 2006).

1.4.2.2. Wet deposition

Scavenging of heavy metals by precipitation processes deposit heavy metals on land or water (Durnford *et al.*, 2010). Some metals are deposited right at the point at which they

are released into the atmosphere whereas others found in aerosols are much lighter and can travel longer distances further away from the source (Kanellopoulou, 2001). The fate and effect of heavy metals deposited by precipitation and dry deposition include ecotoxic effects in the receiving land, water, animals and plants (Figure 4). According to Cizmecioglu and Muezzinoglu (2008), the fraction of heavy metal that reaches the collector is water soluble and the anthropogenic sources of these heavy metals are typically in water soluble forms.

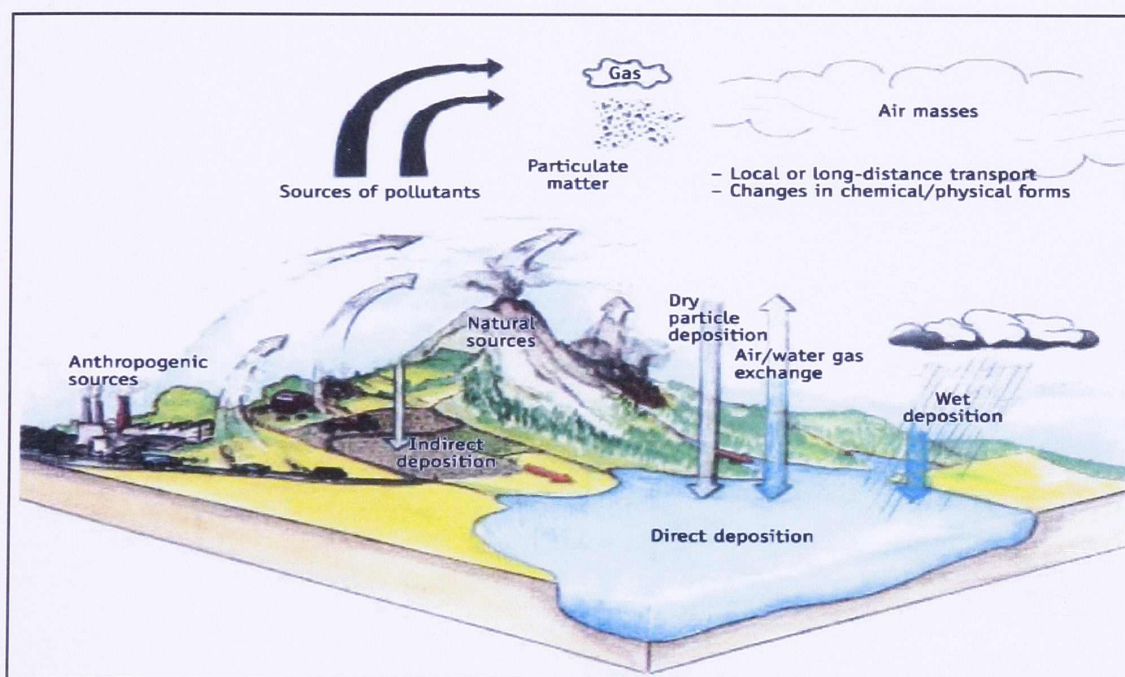


Figure 4. Atmospheric deposition of pollutants (Stolzenbach, 2005)

1.5. Heavy metals in the aquatic environment

Waterways are susceptible to heavy metal pollution from point and non-point source sites (http, 3). In areas where there is surface water, the air-gas exchange of pollutants is especially important for wet and dry deposition (Reinfelder *et al.*, 2004). In addition, heavy metal leachate from waste dump sites cause contamination of local aquifer systems (Banar *et al.*, 2009). Fractured and weathered rocks may allow seepage of water into the groundwater and may eventually affect drinking water supplies.

Consumption of aquatic organisms found in areas contaminated with toxic metals may cause a health hazard to consumers (Miretzky, 2004). Obviously, in many circumstances pollutants may pass through a variety of urban and natural compartments and processes following atmospheric deposition before reaching water systems (Priadi, 2008). However, the effects on water quality may be directly related to the concentration of pollutants released from the air.

1.6. Heavy metals in soils and vegetation

Heavy metals can persist in soils for longer periods of time than other environmental compartments (Lasat, 2002; Padmavathiamma *et al.*, 2008). While soils near roadways are highly susceptible to heavy metal contamination by transportation, vegetation acts as a sink for these metals by readily intercepting deposition from the atmosphere (Sharma and Prasad, 2010). Other sources can be found in areas where agriculture (fertilizers) and waste incineration sites are found (Onder *et al.*, 2007). Although long range transport may make it difficult to estimate background levels of trace elements in the soil, it is known that contamination of soil mostly occurs in regions where industrial facilities, motor vehicles and municipal waste sites are concentrated.

1.7. Essential and non-essential heavy metals

Most heavy metals are essential at low levels. Intake of these metals is vital to the proper functioning of living organisms. As a matter of fact, development and survival of living organisms depend on some metal ions. Metals like zinc, copper, cobalt, manganese, molybdenum, calcium, potassium, sodium and iron are all considered essential metals for humans. Copper and zinc are considered essential for plant growth and development and are constituents of many enzymes and proteins (Hall, 2001). Unfortunately, some essential metals may be toxic at high concentrations. In certain areas where anthropogenic activities are prevalent, atmospheric deposition of heavy metals can provide either nutrients to ecosystems or toxic substances to the underlying environmental compartments (Galy-Lacaux *et al.*, 2009). Non-essential metals however, have not been identified to serve a specific biological function. Some of these metals include lead and arsenic and their intake may lead to death. Plants and animals are

highly susceptible to the toxicity of non-essential metals like Cd which has been known to cause poisoning to humans (Rashad and Shalaby, 2007).

1.7.1. Heavy metal toxicity

High intake of heavy metals has detrimental effects on animals and humans exposed to them. Scientists have tied the risk of diabetes to exposure to heavy metals such as lead and arsenic (Hyman, 2010). When metals bind to sulfhydryl groups in proteins they may displace essential elements, disrupt functioning or inhibit sulfhydryl group activity leading to toxicity (Hall, 2002). Heavy metals such as arsenic, lead, mercury, cadmium, copper, gold, cobalt and zinc may be very toxic and relatively highly accessible to living organisms. Plants may show various signs of toxicity depending on the type of metal and the type of plant. Generally, in plants they may cause damage to root systems, disrupt the proper functioning of the stomata and inhibit growth (Onder *et al.*, 2007). In humans, heavy metal toxicity may range from reproductive defects to long term lung damage (Gidlow, 2004; ATSDR, 2008). The details of the four toxic heavy metals are discussed as follows:

1.7.1.1. Lead (Pb)

In areas where zinc and gold deposits are found in the environment, one can usually find lead as a contaminant (http 4). In 1970, the federal government was compelled to ban lead in motor vehicular fuel in the United States under the Clean Air Act (Miodovnik, 2011). Lead's ability to replace calcium in the body is perhaps the primary cause of toxicity to humans (Lidsky and Schneider, 2003). According to the EPA (2010), lead is considered a part of the criteria air pollutants and can enter the environment through industrial sources, motor vehicles and plumbing materials that may contaminate water sources. For drinking water the Maximum Contamination Level (MCL) for lead is 0.015 mg/l (Csuros and Csuros, 2002). Soils near roadways, waste incineration sites and hazardous waste sites usually contain lead even today (ATSDR, 2007). Lead may cause numerous toxic defects some of which are listed in Table 3.

Table 3. Concentration and health defects of lead in the blood and health defects (ATSDR, 2007).

Age	Effect	Blood lead ^a (µg/dL)
Children	Depressed ALAD	<5
Children	Neurodevelopmental effects	<10
Children	Sexual maturation	<10
Children	Depressed vitamin D	>15
Children	Elevated EP	>15
Children	Depressed NCV	>30
Children	Depressed hemoglobin	>40
Children	Colic	>60
Adults (elderly)	Neurobehavioral effects	>4
Adults	Depressed ALAD	<5
Adults	Depressed GFR	<10
Adults	Elevated blood pressure	<10
Adults	Elevated EP (females)	>20
Adults	Enzymuria/proteinuria	>30
Adults	Peripheral neuropathy	>40
Adults	Neurobehavioral effects	>40
Adults	Altered thyroid hormone	>40
Adults	Reduced fertility	>40
Adults	Depressed hemoglobin	>50

^a Concentration range associated with effect

ALAD = δ-aminolevulinic acid dehydratase; EP = erythrocyte protoporphyrin; GFR = glomerular filtration rate; NCV = nerve conduction velocity; ND = no data

1.7.1.2. Arsenic (As)

Arsenic is a highly toxic heavy metal found in the environment as As (III) and As (V) (Mumford *et al.*, 2007). Recently its behavior and fate in the environment has gained increasing attention as millions of people become exposed to it everyday (Meharg and Hartley-Whitaker, 2002). In the United States many farmers still use pesticides that contain arsenic. Its use as a herbicide and an insecticide on agricultural land has caused massive amounts of land in the U.S. to become contaminated (Roberts *et al.*, 2006). Farm crops are primarily exposed to arsenic. In certain areas rice and grains have been grown in contaminated soils from arsenic pollution (He *et al.*, 2007). Additionally, researchers have found high levels of arsenic in fields where poultry waste had been applied (Nachman *et al.*, 2005).

Arsenic may also contaminate water sources (ground or surface) through the process of leaching. Most arsenic that is found in the soil would ultimately end up in the water (ATSDR, 2007). When arsenic enters the environment by way of pesticide application, it

may travel from one place to the other through underground water seepage. This action of leaching may ultimately cause pesticides to reach areas like groundwater aquifer systems and large bodies of surface water. According to Csuros and Csuros (2002), the Maximum Contamination Level for arsenic in drinking water is 0.05 mg/l.

Arsenic may enter the body of animals or humans through inhalation, ingestion or absorption through the skin (Figure 5). It may be stored in organs like the brain, bones, or tissues. Long term exposure to arsenic can cause non-cirrhotic portal hypertension and hepatic fibrosis in the liver (Rana *et al.*, 2010). It has been associated with forms of cancer in the skin, lungs, prostate and bladder (Dong, 2002). It can also cause severe health impacts through developmental neurotoxicity which is a serious public health concern (Grandjean and Murata, 2007).

The trivalent form of arsenic which is the most toxic form, can bind to thiol groups. It's neurotoxic effects include inhibiting pyruvate dehydrogenase, the enzyme involved in converting pyruvate to acetyl-CoA, and binding to sulfhydryl groups of dihydrolipoamide (Marcus, 2010). Inhibition of pyruvate dehydrogenase would eventually mean that acetyl-CoA would not be produced and the neurotransmitter acetylcholine may not be released in the cholinergic neuron. In addition to disruption of the pyruvate pathway, the succinate pathway is also disrupted, causing a net result of blockage of the Krebs cycle and interruption of oxidative phosphorylation (Dyro, 2010). One major result of this process is a marked decrease in ATP production. Finally, cellular glucose uptake, fatty acid oxidation and gluconeogenesis may be blocked causing cellular oxidative damage (Marcus, 2010).

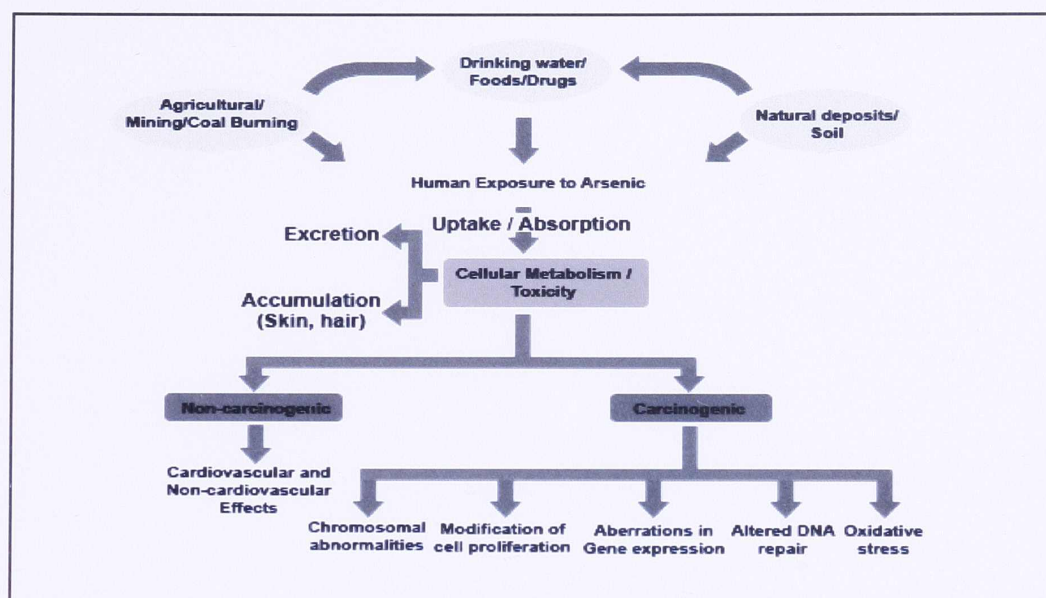


Figure 5. Sources of human exposure and modes of toxicity of arsenic (Roy & Saha, 2002).

1.7.1.3. Cadmium (Cd)

Cadmium is a readily available metal in the environment. It is released into the atmosphere from mining, coal burning and other industrial sources and can travel long distances before falling to the ground (Mohamad and Latif, 2010). Cadmium may also be released into the atmosphere through tobacco smoke. A significant amount of cadmium released by tobacco smoke is absorbed into the blood (Zeneli *et al.*, 2009). Furthermore cadmium poisoning through inhalation of burning fossil fuel and battery manufacturing particles may lead to lung cancer (Andrew *et al.*, 2003). According to Csuros and Csuros (2002), the Maximum Contamination Level for Cadmium is 0.005 mg/l.

Cadmium ranks as one of the most toxic metals to plants and humans (John *et al.*, 2008). It has been linked to kidney damage in the human body (Satarug *et al.*, 2010). Cadmium has very distinct neurotoxic effects in the body (Table 4). It has been known to target and inhibit specific enzymes in the body that are vital to repairing damaged DNA (Tillet, 2010).

Table 4. Toxic effects of cadmium exposure on human health (ATSDR, 2008).

Recipient of Poisoning	Effect
Adults	Breathing air with very high levels of cadmium can severely damage the lungs and may cause death. Breathing air with lower levels of cadmium over long periods of time (for years) results in a build-up of cadmium in the kidney, and if sufficiently high may result in kidney disease.
Children	<p>The health effects seen in children from exposure to toxic levels of cadmium are expected to be similar to the effects seen in adults (kidney, lung, and intestinal damage depending on the route of exposure). Harmful effects on child development or behavior have not generally been seen in populations exposed to cadmium, but more research is needed. A few studies in animals indicate that younger animals absorb more cadmium than adults. Animal studies also indicate that the young are more susceptible than adults to a loss of bone and decreased bone strength from exposure to cadmium.</p> <p>Cadmium is found in breast milk and a small amount will enter the infant's body through breastfeeding. The amount of cadmium that can pass to the infant depends on how much exposure the mother may have had.</p>

1.7.1.4. Chromium (Cr)

Chromium is a transition element that exists in the environment in two valence states, trivalent chromium or Cr (III) and hexavalent chromium or Cr (VI) (Qi *et al.*, 2000). In the air, chromium emissions are typically trivalent in the form of small particles and aerosols (United States EPA, 2000). It may be released into the atmosphere predominantly through human activities. Workers in chrome production, chrome plating and stainless steel welding industries receive high levels of exposure to Chromium (VI), a known carcinogen (Stout *et al.*, 2009). Other sources of chromium include cement-producing plants, automobile brake lining, catalytic converters for automobiles, leather tanneries, and chrome pigments (United States EPA, 2000).

Toxicity of chromium causes shortness of breath, coughing, decreased pulmonary function and other respiratory effects with chronic and acute exposure (Caglieri *et al.*, 2006). Inhalation of chromium particles in the air is a primary route of toxicity to the lungs. Furthermore, chromium found in water used for farming crops and livestock is

especially damaging to humans and animals. The maximum contamination level is 0.10 mg/l (Csuros and Csuros, 2002).

1.8. Air Quality in Georgia

The state of Georgia is one of the most rapidly growing states in the country. Atlanta, Georgia, is home to the world's busiest airport, the Hartsfield-Jackson International Airport (Yee, 2007). While air transportation is a valid concern for air pollution, the EPA recently reported that the high air pollution levels detected in the Georgia valley vicinity may be due to diesel and wood burning in the area (Aujla, 2010).

The Georgia Environmental Protection Division (GEPD) has been monitoring approximately 200 air pollutants over a period of thirty years across the state of Georgia (GADNR, 2009). Air pollution monitoring sites have been set up in specific regions across the state in order to satisfy the requirements outlined by the Clean Air Act (Figure 6).

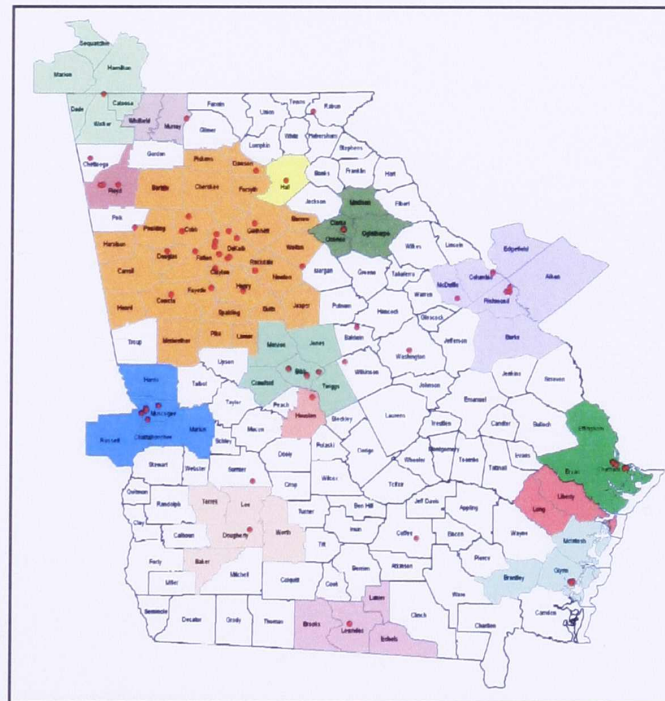


Figure 6. Air pollution monitoring sites in Georgia (GADNR, 2009)

Under Clean Air Act provisions, heavy metals such as Pb, Cd, Cr and As are placed in the category of air toxics or Hazardous Air Pollutants also known as HAPS (U.S. EPA, 2010). The Georgia Department of Natural Resources (GADNR) has been specifically monitoring some of these heavy metals for several years. Some of the monitoring sites are located in areas like Columbus, Warner Robins, South Dekalb and Valdosta in the state of Georgia (Figure 7).

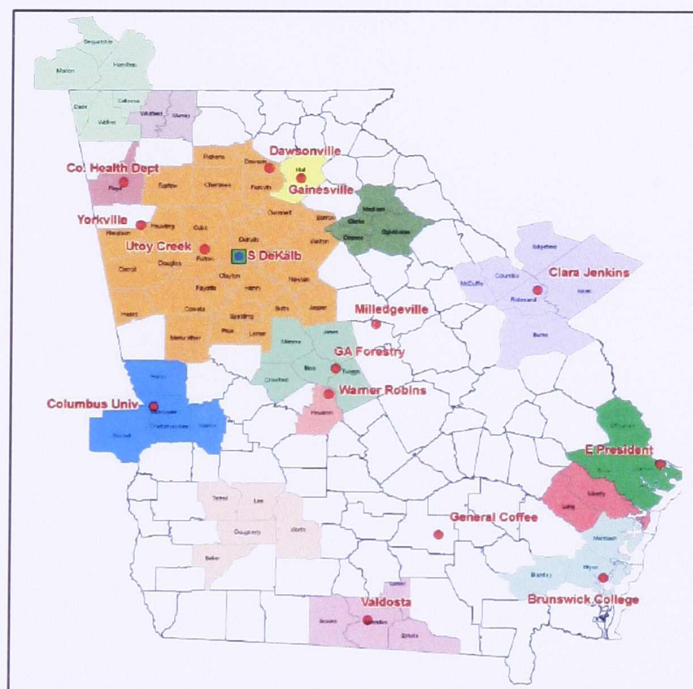


Figure 7. Heavy metal monitoring sites in Georgia (GADNR, 2009)

1.8.1. Description of study area

Columbus is located at 32°29'23" N and 84°56'26" W in the south eastern region of the United States of America (Figure 8). It is approximately 100 miles down valley from Atlanta, the capital of the state of Georgia. Columbus has a population of about 189,885 people (U.S Census Bureau, 2009). In the year 2000, the U.S Census Bureau reported that the city of Columbus, Georgia, was approximately 560,110 km² in size. Currently, it may be regarded as one of the fastest developing cities in the state of Georgia. This is due to the fact that industries are continuing to expand to meet the growing population demands created by the influx of residents into the neighboring Fort Benning Military Base.

A number of industries are located in Columbus including textile mills, food, primary metal manufacturers, manufacturing of parts for slurry mixers, a blind factory, a tile company, the Cessna Corporation (an aircraft manufacturing facility) and McCauley Propeller Systems. In addition to these industries, the Columbus area is home to the Columbus Metropolitan Airport located in close proximity to the sampling site (~ 3.72 km). Hazardous waste incineration facilities are located about 313.82 km from the sampling area along I-75N ([http, 5](http://5)).

A major highway known as Manchester Expressway is also located approximately 0.24 km away from the sampling area. Heavy motor vehicular traffic may frequent this highway between the hours 7:00 am and 9:00 am in the morning, 12:00 pm and 1:30 pm during the day and between 3:30 pm and 6:00 pm during the afternoon.

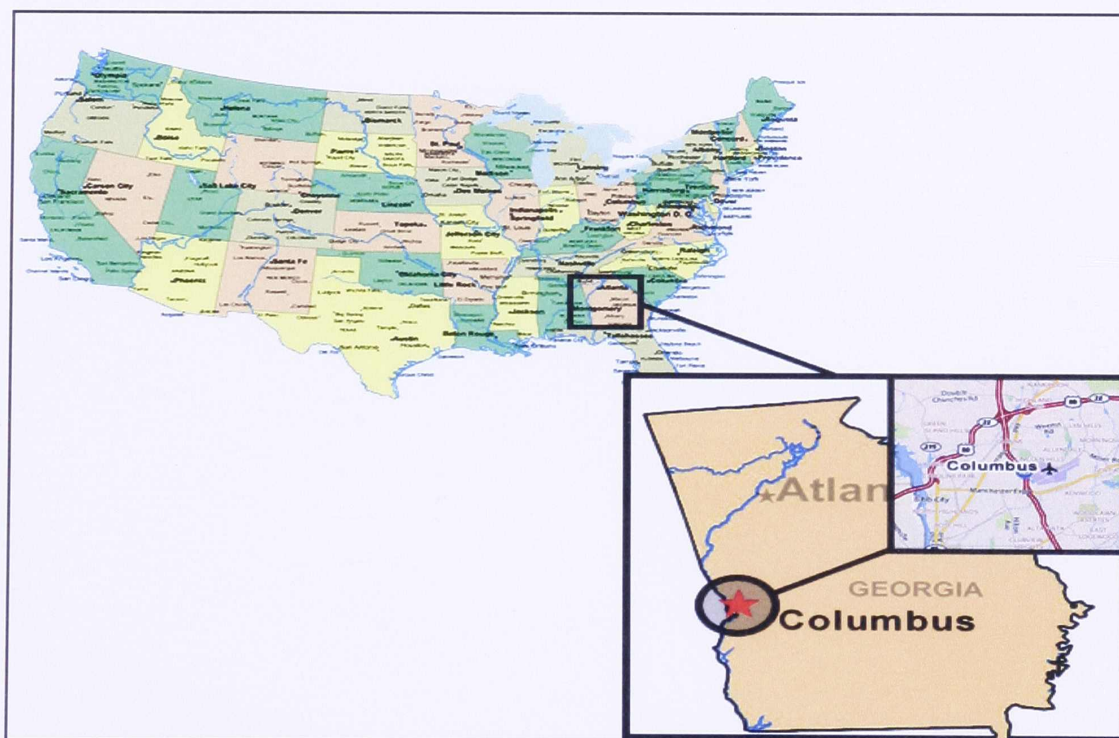


Figure 8. Location of Columbus, Georgia in the United States

1.8.2. Climatology

The Columbus, Georgia, region has subtropical climate. Throughout the year the temperature is generally humid, with consistent rainfall specifically during the late

spring and summer months. Table 5 and 6 show the climatic records for Columbus in 2009 and 2010 to 2011, respectively ([http, 6](#)). According to these climatology reports, maximum temperature averages during the summer months reached 32.22°C whereas averages during the winter months were as high as -1.11°C. During the summer, thunderstorms may increase the humidity of the area. Alternately, during the winter season which is the driest of all the four seasons there may be an increased chance of snowfall accumulation. The latter event may be rare.

Table 5. 2009 Climatology report for Columbus, Georgia ([http, 6](#))

Month	Ave. High (°C)	Ave. Low (°C)	Mean (°C)	Ave. Precip. (mm)
January	13.88	2.77	8.33	121.41
February	16.66	3.88	10	113.79
March	20.55	7.77	14.44	145.05
April	25	11.11	17.77	97.536
May	28.33	16.11	22.22	91.948
June	32.22	20.55	26.11	89.154
July	33.33	22.22	27.77	128.016
August	32.77	21.66	27.22	96.012
September	30	18.88	24.44	77.978
October	25	12.77	18.88	59.182
November	20	7.77	13.88	100.838
December	15	3.88	9.44	111.76

Table 6. 2010-2011 Climatology report for Columbus, GA ([http, 6](#))

Month	Ave. high (°C)	Ave. low (°C)	Mean (°C)	Ave. Precip. (mm)
2010				
January	10.88	-0.179	5.48	4.69
February	11.41	0.278	6.012	3.77
March	17.49	5.09	11.42	3.47
April	26.15	11.15	18.77	1.46
May	29.86	18.15	24.16	5.92
June	33.61	22.69	28.26	2.22
July	35.29	23.66	29.66	1.89
August	34.93	24.37	29.78	2.59
September	30.53	20.19	27.16	2.89
October	27.38	12.60	20.16	1.30
November	20.72	7.50	14.30	3.88
December	11.92	0.036	6.11	1.58
2011				
January	11.81	1.093	6.56	2.86
February	18.15	5.079	11.75	4.23
March	21.81	49.26	15.81	4.34

The GEPD has assembled a variety of information on toxic metal concentrations at various monitoring sites in the state of Georgia. Towns such as Macon and Savannah, Georgia, have shown a marked increase in heavy metals concentration from the years

2008 to 2009 (Figure 9a). On the contrary, in areas like Dawsonville and Yorkville a decrease in heavy metals concentration was observed from 2008 to 2009.

According to the GEPD, metals including Cr, Cd, and Pb showed higher concentrations from 2005 to 2008 across all monitoring sites in Georgia (Figure 9b). Zinc had the highest concentration average over a 5 year span followed by manganese, lead, chromium and nickel (GADNR, 2009). The GEPD suggested that high levels of some of these metals over the past years may be attributed to the use of vehicles on roadways.

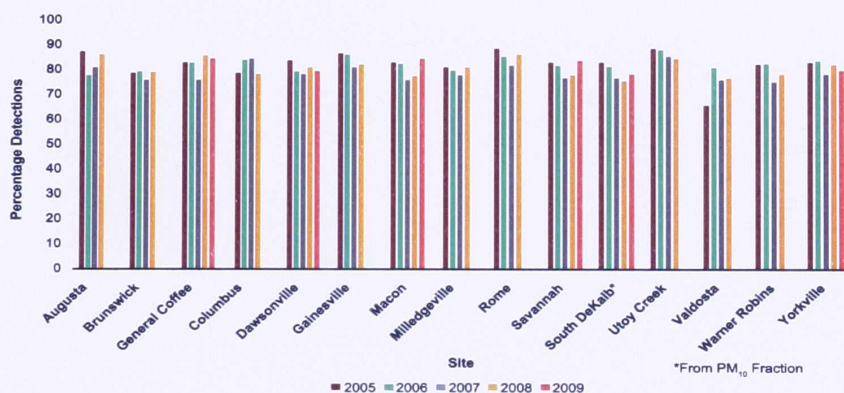


Figure 9a. Percent metal detection at air quality monitoring sites in Georgia from 2005-2009 (GADNR, 2009).

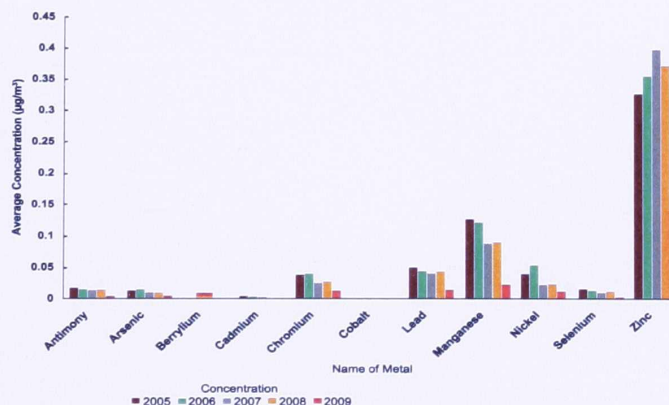


Figure 9b. Percent metal detection and average concentration of metal species at monitoring sites from 2005-2009 (GADNR, 2009).

In 2005, lead emissions were at its highest in Georgia (Figure 9b). The EPA suggested that fossil fuel combustion, non road equipment and industrial processes were the three

primary causes for the increase in lead emissions during that time as illustrated in Figure 10 ([http 7](#)).

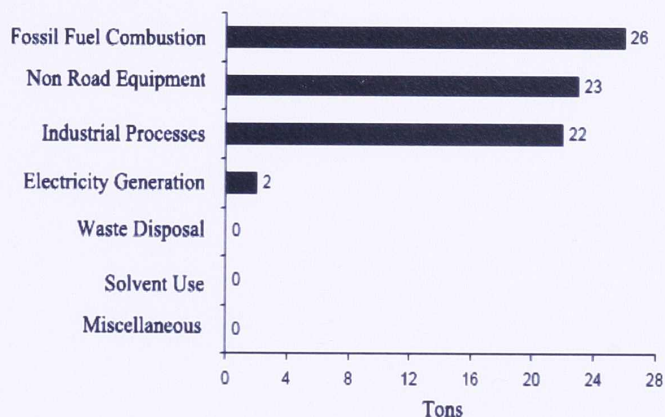


Figure 10. Lead emissions in the state of Georgia in 2005 ([http 7](#); GADNR, 2009)

Prior to this work, limited studies had been conducted on heavy metal pollution in the environment in Columbus, Georgia. Apart from GADNR's ambient air monitoring program, studies have been ongoing on investigating heavy metal pollution in children's environments in Columbus, GA. Results from this study will be compared to similar studies across the U.S. and abroad which focused on atmospheric deposition of heavy metal pollutants like Cd, Cr, As and Pb in ambient air and wet deposition.

Chapter 2: Methodology

2.1. Sampling site selection

The sampling site selected for this research was the roof top of the Frank G. Lumpkin Jr. Center, on Columbus State University's main campus in Columbus, GA, (Figure 11). Sampling was conducted at an elevation of 107.6 meters. This site located south from a major expressway known as Manchester Expressway ($32^{\circ} 30' 15''$ N, $84^{\circ} 56' 26''$ W). It was chosen based on accessibility, safety, and representativeness (Melaku *et al.*, 2007).



Figure 11. Ambient air and wet deposition sample collection site (Google Earth Maps, 2010)

2.2. Sampling

2.2.1. Ambient air samples

Ambient air samples were collected using a cyclone impactor which was deployed on the roof top of the Lumpkin building. A total of 73 ambient air samples were collected between January 17, 2010 and March 28, 2011. Ambient air samples were collected every 6 days over a 15 month observation period on 9 cm diameter glass fiber filters (Fisher Scientific, USA) in the multi-stage cyclone impactor. Glass fiber filters were 0.32 mm thick, with a particle retention of 1.5 μ m. They were weighed prior to and after sampling. The average air volume sampled over a 6 day sampling period was 65,315 l at a flow rate of 0.126 l/s. The details of the ambient air sampling can be found elsewhere (Melaku *et al.*, 2007).

2.2.2. Wet deposition samples

A Total Precipitation Collector, TPC-3000, (Yankee Environmental System, YES) was also deployed a few meters away from the multi-stage cyclone impactor. A total of 53 wet deposition samples were collected between January 15, 2010 and March 28, 2011. The collection bucket on the TPC-3000 was pre-washed with Deionized water (3 times) followed by 0.14M HNO₃ (2 times) to minimize contamination. After precipitation events, wet deposition samples were poured into a large 1000 ml narrow mouth high density polyethylene (HDPE) bottles and transferred to the laboratory. In the laboratory, some of the sample collected was transferred from the large HDPE bottle to a small 125 ml HDPE bottle and 2 drops of 0.14 M HNO₃ was added. The details of the wet deposition sampling can be found elsewhere (Melaku *et al.*, 2007).

2.3. Sample pretreatment

Ambient air samples collected on pre-weighed glass fiber filters were tightly sealed in aluminum foil and a zip lock bag and transported to the laboratory where they were weighed again and stored in a refrigerator at 4°C until further analysis. For the pretreatment of wet deposition samples, 2 drops of concentrated nitric acid was added to

each sample immediately after collection and samples were stored in a refrigerator at 4°C until further analysis.

Aqua regia digestion method was used to extract heavy metals in ambient air samples and standard reference materials (Cizmecioglu & Muezzinoglu, 2008; Melaku *et al.*, 2007). Sample preparation was conducted underneath a pre-cleaned laboratory hood to ensure a safe environment and minimize contamination. For the aqua regia digestion, concentrated nitric acid (Acros Organics, of 68-70% solution in water, ACS reagent grade) and 37% Hydrochloric acid (Sigma-Aldrich) were used. After transferring the filters and 28 ml aqua regia into a teflon beaker, the beakers were covered and allowed to digest for a total of 16 hours at room temperature. After 16 hours, the teflon beakers were placed on a hot plate and allowed to digest at 130°C for approximately 2 hours under reflux conditions. Then the beakers were allowed to cool to room temperature. Subsequently, digested samples were filtered using ashless Whatman filter paper (90 mm, Grade 42; Fisherbrand, Fisher Scientific) and the volume was made to 100 ml using 0.14M HNO₃. The final volume of sample collected in a graduated cylinder was poured into small 125 ml HDPE bottles and stored at 4°C until analysis.

2.4. Reagents and Standards

Analytical grade reagents were used throughout this study. Deionized water from a Milli-Q, Millipore purification system was used (Millipore, USA). For the aqua regia, 7 ml of concentrated nitric acid (Acros Organics, 68-70% solution in water, ACS reagent grade) and 21 ml of 37% Hydrochloric acid (Sigma-Aldrich) were used.

2.5. Instrumentation

Sample analysis was done using a Shimadzu Atomic Absorption Spectrophotometer, AA-7000 series instrument. This instrument is equipped with a Graphite furnace and a Flame unit which can both be used to determine the concentration of a specific analyte (Figure 12). It is also equipped with a Graphite furnace auto sampler system. This research required the use of Graphite Furnace unit in order to measure concentrations of the heavy metals at parts per billion (ppb) levels (Uygur *et al.*, 2010).

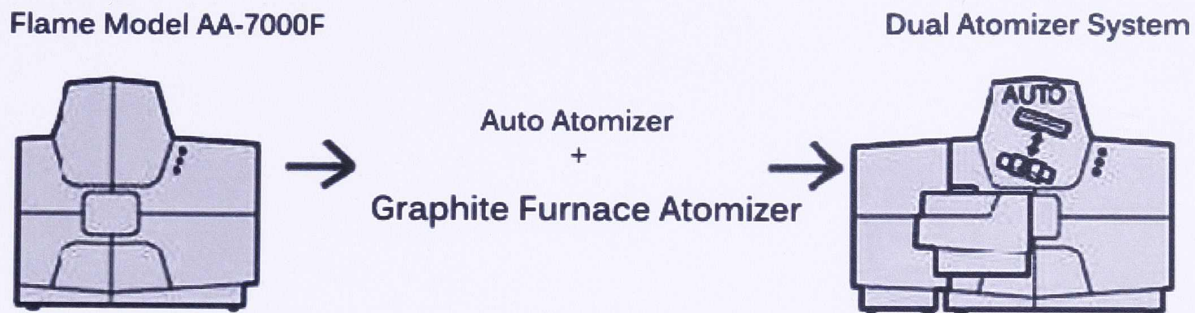


Figure 12. GFA-7000 with Flame and Graphite Furnace Units ([http, 8](http://8))

2.6. Calibration

Calibration standards were prepared from 1000 ppm stock solutions of lead, chromium, cadmium and arsenic. 0.14M of nitric acid was used to dilute standard solutions (Melaku *et al.*, 2005). The unknown metal concentrations in the samples were determined from calibration curves that were constructed through the Wizzard AA computer program with known concentrations of the heavy metals (Muezzinoglu and Cizmecioglu, 2006).

2.7. Determination of Pb, Cr, As and Cd Using GF-AAS

Determination of trace metal concentrations in environmental samples can be achieved by the use of the highly sensitive Graphite Furnace Atomic Absorption Spectrometer (GF-AAS) technique (Uygur *et al.*, 2010). Elemental analysis by AAS involves separating free atoms from elements of interest (Csuros and Csuros, 2002). In order to measure and determine the presence of specific elements, free atoms of the element must be transferred from a ground state to an excited state (Figure 13.). This can be done by either flame or graphite furnace atomic absorption techniques. For flame, the maximum temperature used to irradiate free atoms of an element is 2700°C and for graphite furnace atomic absorption the maximum temperature is 3000°C. In this study, the GF-AAS was used to excite free atoms (Fifield and Haines, 2000).

The temperature program of GFAAS involves three major steps. The first is drying, the second pyrolyzing and the third atomizing. To achieve these three phases each sample must be run through a multi-step temperature program. During the drying phase the

samples usually undergo low temperatures of about 100°C to 120°C. After this step and prior to atomization the furnace is cooled down. Then, the atomization step allows the molecules of the sample to dissociate due to increased temperature. A vapor of the analyte is produced by this atomization process. After the process of atomization, the temperature inside the burner is increased so as to burn out any sample left in the graphite tube. Subsequently, a cooling down phase allows the furnace to return to ambient temperature before another sample could be introduced. Schematic diagram of atomic absorption is presented in Figure 14.

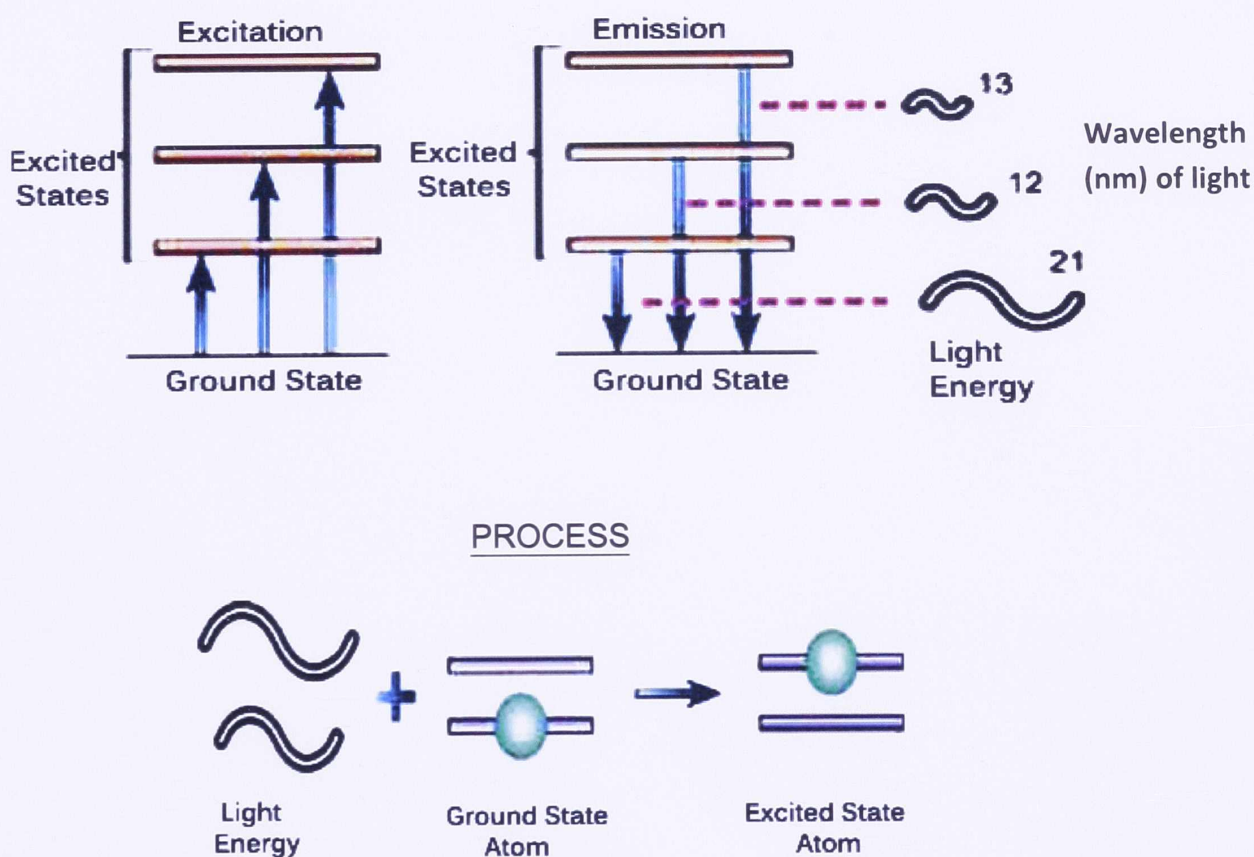


Figure 13. Atomic absorption theory ([http, 9](http://9))

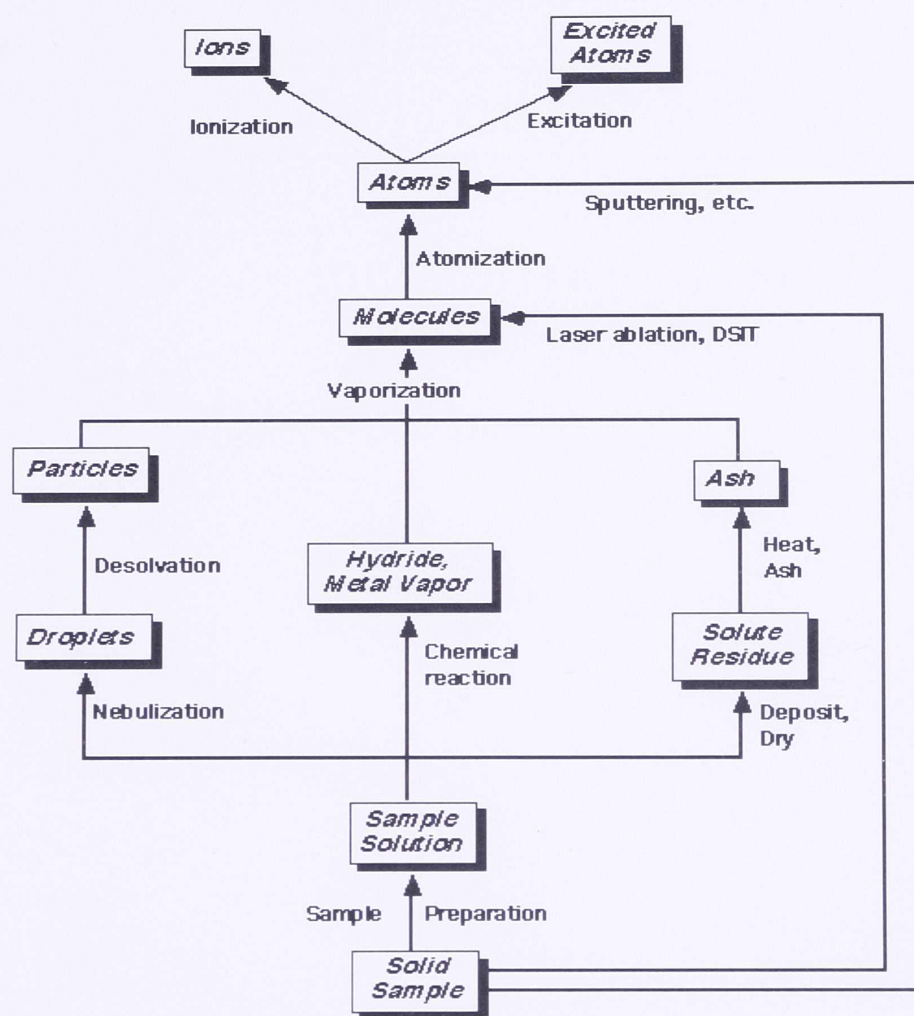


Figure 14. Atomic Absorption Spectroscopy (Hieftje, 2005)

Chapter 3: Results and Discussion

3.1. Optimization of ashing and atomization temperatures

The ashing and atomization temperatures were optimized for cadmium, chromium, arsenic and lead. The optimized temperature programs used in this study are presented in Table 7. Temperature programs were used to dry, pyrolyze and atomize wet deposition and ambient air samples in order to determine the concentrations of heavy metals within the samples. In RAMP modes, temperatures were increased within a variable time (Csuros and Csuros, 2002). On the other hand, in STEP modes, the furnace was initially heated to a target temperature, and the temperature was maintained until the end of the stage (http, 10). Temperatures were increased in such a way as to prevent sample loss prior to the atomization stage.

Table 7. Temperature Programs

Cadmium Furnace Program

Stage	Temp ° C	Time (s)	Mode	Sens.	Ar flow rate (L/min.)
1	120	20	RAMP		1.00
2	250	10	RAMP		1.00
3	300	10	STEP		1.00
4	300	3	STEP	✓	0.00
5*	1500	3	STEP	✓	0.00
6	2200	3	STEP		1.00

* ; Atomization Stage: ✓ ; Pyrolysis and Atomization Temperatures

Chromium Furnace Program

Stage	Temp ° C	Time (s)	Mode	Sens.	Ar flow rate (L/min.)
1	60	3	RAMP		0.10
2	120	20	RAMP		0.10
3	250	10	RAMP		0.10
4	800	10	RAMP		1.00
5	800	10	STEP		1.00
6	800	3	STEP	✓	0.00
7*	2300	3	STEP	✓	0.00
8	2500	2	STEP		1.00

Arsenic Furnace Program

Stage	Temp ° C	Time (s)	Mode	Sens.	Ar flow rate (L/min.)
1	120	20	RAMP		0.10
2	250	10	RAMP		0.10
3	600	10	RAMP		1.00
4	600	10	STEP		1.00
5	600	3	STEP	✓	0.00
6*	2200	3	STEP	✓	0.00
7	2500	2	STEP		1.00

Lead Furnace Program

Stage	Temp ° C	Time (s)	Mode	Sens.	Ar flow rate (L/min.)
1	60	3	RAMP		0.10
2	120	20	RAMP		0.10
3	250	10	RAMP		0.10
4	700	10	RAMP		1.00
5	700	10	STEP		1.00
6	700	3	STEP	✓	0.00
7*	2000	3	STEP	✓	0.00
8	2500	2	STEP		1.00

3.2. Limits of Detection (LOD)

The limits of detection are used to determine the presence of the elements (Thomsen *et al.*, 2003). It can be defined as the concentration that will produce an absorbance signal twice the standard deviation of the blank (Csuros and Csuros, 2002). The LODs for Cd, Cr, As and Pb in wet deposition and ambient air are presented in Table 8. The LOD for Pb in wet deposition was 0.054 µg/l, which was comparable to 0.08 µg/l reported in wet deposition by Chen *et al.* (2005) using GF-AAS. The detection limit for Cd in wet deposition in this study was 0.05µg/l, compared to the LOD of 0.057 µg/l reported in wet deposition by Melaku *et al.* (2007), using GF-AAS. LODs for Cr and As in wet deposition in this study were comparable to values of 0.39 µg/l (Cr) and 0.003 µg/l (As) obtained in wet deposition in other studies using electrothermal atomic absorption spectrometry (ETAAS) and GF-AAS, respectively (Table 8).

Table 8. Limits of Detection

Heavy Metal	Wet Deposition ($\mu\text{g/l}$)	Ambient Air ($\mu\text{g/l}$)	Other Literature WD ($\mu\text{g/l}$)
Pb	0.054	0.110	0.08, Chen <i>et al.</i> , 2005
Cd	0.050	0.128	0.057, Melaku <i>et al.</i> , 2007
Cr	0.048	0.140	0.39, Stasinakis <i>et al.</i> , 2003
As	0.012	0.161	0.003, Liang <i>et al.</i> , 1998

3.3. Validation of the analytical procedures

Standard Reference Materials (SRMs) obtained from the National Institute of Standard and Technology (NIST) were used to validate all the analytical procedures used for the analysis of heavy metals in ambient air and wet deposition samples in this study. Table 9 shows the validation results for SRM 8704 (Buffalo River Sediment), SRM 2586 (Trace Element in Soil Containing Lead from Paints), SRM 1648a (Urban Particulate Matter), and SRM 1643e (Trace Elements in Water). SRMs were certified by NIST using instrumental neutron activation analysis (INAA) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Our results were in agreement with the certified values of all standard reference materials with a recovery $\geq 94\%$ for all heavy metals.

Table 9. Validation of Procedures

SRM 8704 Buffalo River Sediment (95% CI)

Heavy Metal	This Study, mg/kg	Certified Value mg/kg	% Recovery
As	16 ± 1.7	17	95
Pb	147 ± 20	150 ± 17	98
Cr	123.5 ± 5.5	121.9 ± 3.8	101
Cd	2.98 ± 0.31	2.94 ± 0.29	101

SRM 2586 Trace Elements in Soil Containing Lead from Paints (95% CI)

Heavy Metal	This Study, mg/kg	Certified Value mg/kg	% Recovery
As	8.2 ± 1.8	8.7 ± 1.5	94
Pb	434 ± 20	432 ± 17	100
Cr	304 ± 43	301 ± 45	101
Cd	2.65 ± 0.76	2.71 ± 0.54	98

SRM 1648a Urban Particulate Matter (95% CI)

Heavy Metal	This Study, mg/kg	Certified Value mg/kg	% Recovery
As	117.6 ± 5.3	115.5 ± 3.9	102
Pb	0.653 ± 0.030	0.655 ± 0.033	100
Cr	405 ± 15	402 ± 13	101
Cd	74.1 ± 3.4	73.7 ± 2.3	102

SRM 1643e Trace Elements in Water (95% CI)

Heavy Metal	This Study, µg/L	Certified Value µg/L	% Recovery
As	61.22 ± 0.93	60.43 ± 0.72	101
Pb	19.76 ± 0.40	19.63 ± 0.21	102
Cr	20.51 ± 0.33	20.40 ± 0.24	101
Cd	6.572 ± 0.070	6.568 ± 0.073	100

3.4. Analysis of wet deposition samples

The total heavy metal concentrations for cadmium, chromium, arsenic and lead in wet deposition are reported in five categories. They are: (1) individual trends for 6 day sampling periods, (2) monthly averages over 15 months, (3) seasonal averages which were divided as follows: Winter, 2009 (December 21, 2009 to March 19, 2010), Spring, 2010 (March 20, 2010 to June 20, 2010), Summer, 2010 (June 21, 2010 to September 21, 2010), Fall, 2010 (September 22, 2010 to December 20, 2010) and finally Winter, 2011 (December 21, 2010 to March 19, 2011), (4) correlation analysis between concentrations of heavy metals, and (5) correlation analysis between amount of rainfall (mm) and concentrations of heavy metals. The total amount of rainfall reported over the 15 month sampling period in Columbus, GA was approximately 1279.65 mm (50.38 inches). Concentrations of cadmium, chromium, arsenic and lead in wet deposition ranged from ND (Not detected) - 0.656 µg/l, 0.167 - 98.2 µg/l, ND - 0.911 µg/l and 0.103 - 10.50 µg/l, respectively.

3.4.1. Heavy metal concentration trends in wet deposition

Cadmium concentrations in wet deposition ranged from ND - 0.656 µg/l. Results indicate that concentrations for cadmium in wet deposition exhibited consecutive peaks over the first 25 weeks of sampling, followed by a marked decrease in concentration thereafter until sample WD48 (Figure 15a). As a matter of fact, the maximum

concentration of cadmium in wet deposition, which is 0.656 $\mu\text{g/l}$, was observed in WD48. In addition, the average concentration of 0.096 $\mu\text{g/l}$ for cadmium in wet deposition was found to be significantly lower than the average of 0.48 $\mu\text{g/l}$ reported in wet deposition by Farahmandkia *et al.* (2010) in a high traffic zone in Zanjan, Iran. This may suggest that vehicular traffic may not be the predominant source of cadmium concentrations in this study. A precision (Relative Standard Deviation) of $< 10\%$ was found for approximately 43% of samples.

Concentrations for chromium ranged from ND to 98.2 $\mu\text{g/l}$. The maximum concentration of chromium, which is 98.2 $\mu\text{g/l}$, was observed in WD8 (Figure 15b). This was the single highest concentration value observed for all heavy metals in wet deposition samples which may suggest a predominant source of Cr during the time of sampling. Such sources may include vehicular traffic, construction or other regional sources. Furthermore, this concentration was inconsistent with the findings in the San Francisco Bay area, where a maximum concentration of 0.42 $\mu\text{g/l}$ was observed for Cr in wet deposition ([http, 13](http://www.sfbay.wrri.edu/13)). A precision of $< 10\%$ was found for chromium for 71% of the samples.

Arsenic, on the other hand, was reported at considerably lower concentrations compared to the other three heavy metals. Concentrations for arsenic ranged from ND to 0.9 $\mu\text{g/l}$ for all 53 WD samples (Figure 15c). Spikes in concentration of arsenic were clearly observed in weeks 10, 26, 42 and 52 of sampling. In addition, marginal sample to sample variability was also noticeable indicating that concentrations of arsenic were relatively constant throughout sampling. In this case, a precision of $\leq 10\%$ was found in merely 35% of wet deposition samples.

For lead, concentrations in wet deposition ranged from 0.103 $\mu\text{g/l}$ to 10.50 $\mu\text{g/l}$. Concentrations for the first 30 weeks of sampling were higher compared to the rest (Figure 15d). In fact, high sample to sample variability was evident over the first 30 weeks. This is in agreement with the study by Melaku *et al.* (2007) in the Washington, DC area. Concentrations seemed to decrease after WD30 which is reinforced by the observation that all sample concentration levels remained below the sample mean of

1.28 µg/l thereafter. A precision of < 6% was found for 94% of the samples analyzed for lead.

Particulate matters are typically high in construction areas which are a common source of both cadmium and lead (Norela *et al.*, 2009; [http](#), 11). It is likely that the high concentrations of cadmium and lead could be due to construction activities on Columbus State University's main campus. Construction was initiated in October, 2009 roughly 50 to 60 meters away from the sampling site and ended in the fall, 2010. According to OSHA, ([http](#), 11) Cd may be released into the atmosphere through activities such as wrecking, demolishing and welding on surfaces that are painted with cadmium-containing paints. Tobacco smoke is also a major contributor to cadmium release in the atmosphere. One cigarette contains 0.5 to 2 µg of cadmium and only 10% is inhaled by the smoker ([http](#), 12). Lead, on the other hand, may be a component in older paints, older plumbing hardware, solder, metals, storage batteries, sound and vibration absorbers, lead gasoline, obsolete insecticides (lead arsenate), lead crystal and flint glass. An account of the uses of lead and cadmium in the construction industry may both provide evidence of sources and elucidate the fact that during the time of construction concentrations for both heavy metals in wet deposition were higher than after construction ended.

High traffic areas usually have elevated levels of trace metals in atmospheric deposition due to the degradation of motor vehicular parts containing these elements and the resuspension of road dust (Conko *et al.*, 2004). Traffic areas are sources of lead and chromium. In the atmosphere, Pb can originate from high temperature processes such as fuel combustion (Halstead *et al.*, 2000). As a result, traffic emissions from motor vehicles may be considered a plausible source of lead in wet deposition. Automobile brake lining and catalytic converters for automobiles may be considered major sources of Cr. Manchester Expressway, which is located near the sampling site, has a high frequency of vehicular traffic on a day to day basis. As a result, road dust containing wear from brake lining and catalytic converters may be a source of Cr and Pb to the area. In addition to motor vehicles, construction vehicles such as tractors, trucks and trailers may also be a possible source of heavy metals in wet deposition samples. Welding of chromium plated steel in construction or industrial areas as well as printing facilities,

metallurgic, structural steel, and paint manufacturing may all contribute to Cr concentrations (Wagner-Meinert Inc, 2008; Nguyen and Kim, 2008).

Arsenic is used in fireworks, glass, semiconductor materials, wood preservatives, copper and lead alloys and insecticides (Hardy *et al.*, 2008). Arsenic can also be found in agricultural chemicals. In Muscogee county Georgia, the average size of farmland increased from 161 acres to 179 acres between 2002 and 2007 ([http](#), 14). According to the 2007 Census of Agriculture, 36.78% of farmland in the state is used for crops and 45.65% is woodland. In addition, in 2007 there was an increase in fertilizers and chemicals purchased for farmlands in the state of Georgia (USDA, 2009). As a result, agricultural chemicals may be considered a potential source of As concentrations.

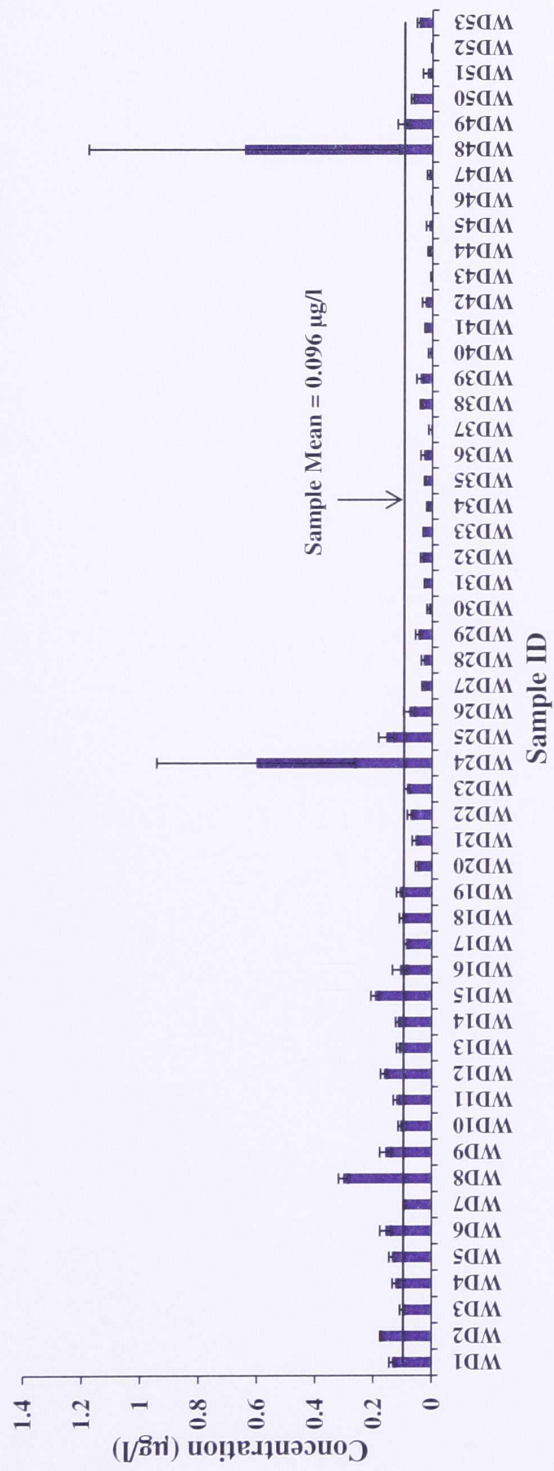


Figure 15a. Concentrations of cadmium in wet deposition

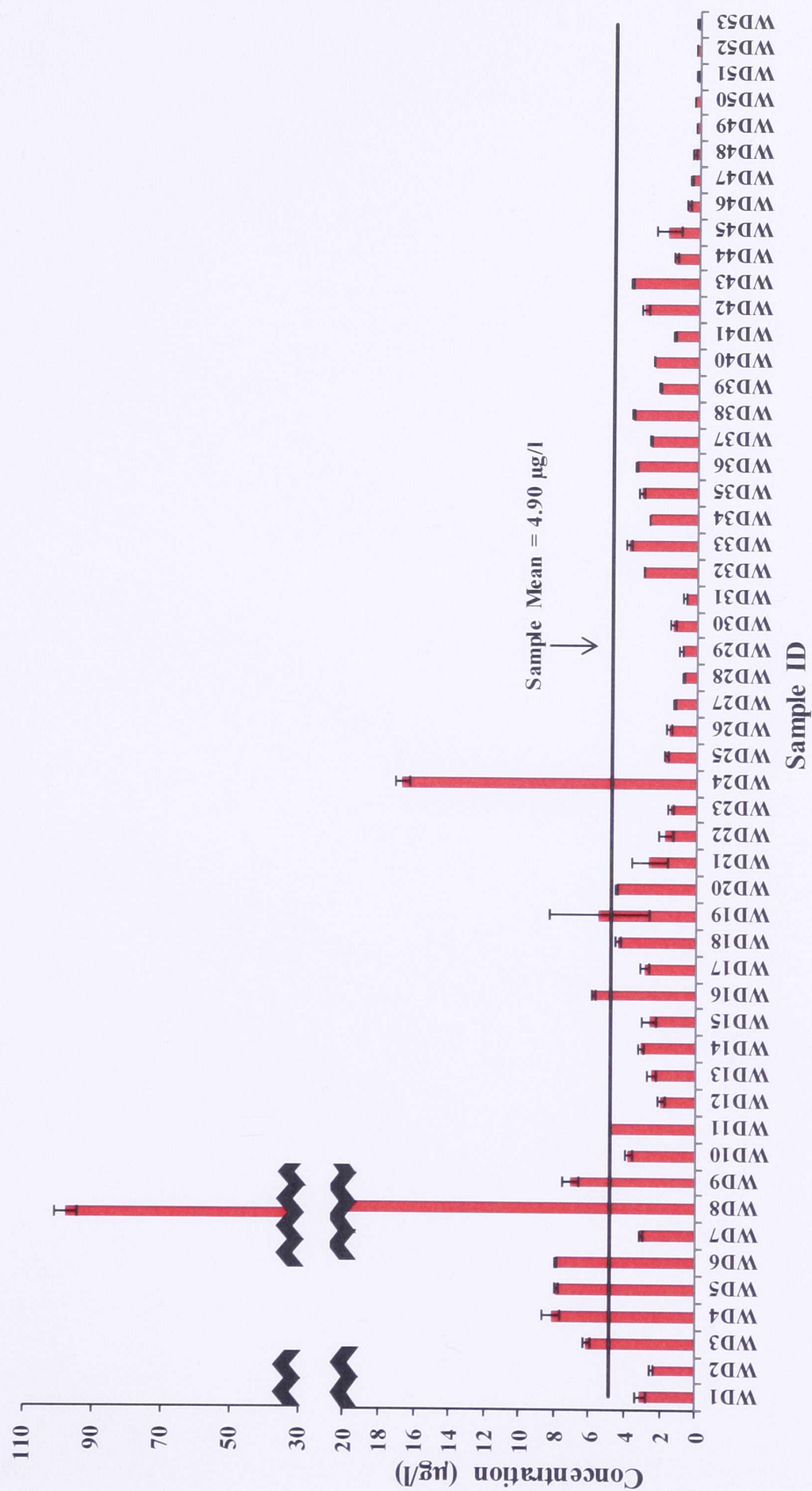


Figure 15b. Concentrations of chromium in wet deposition

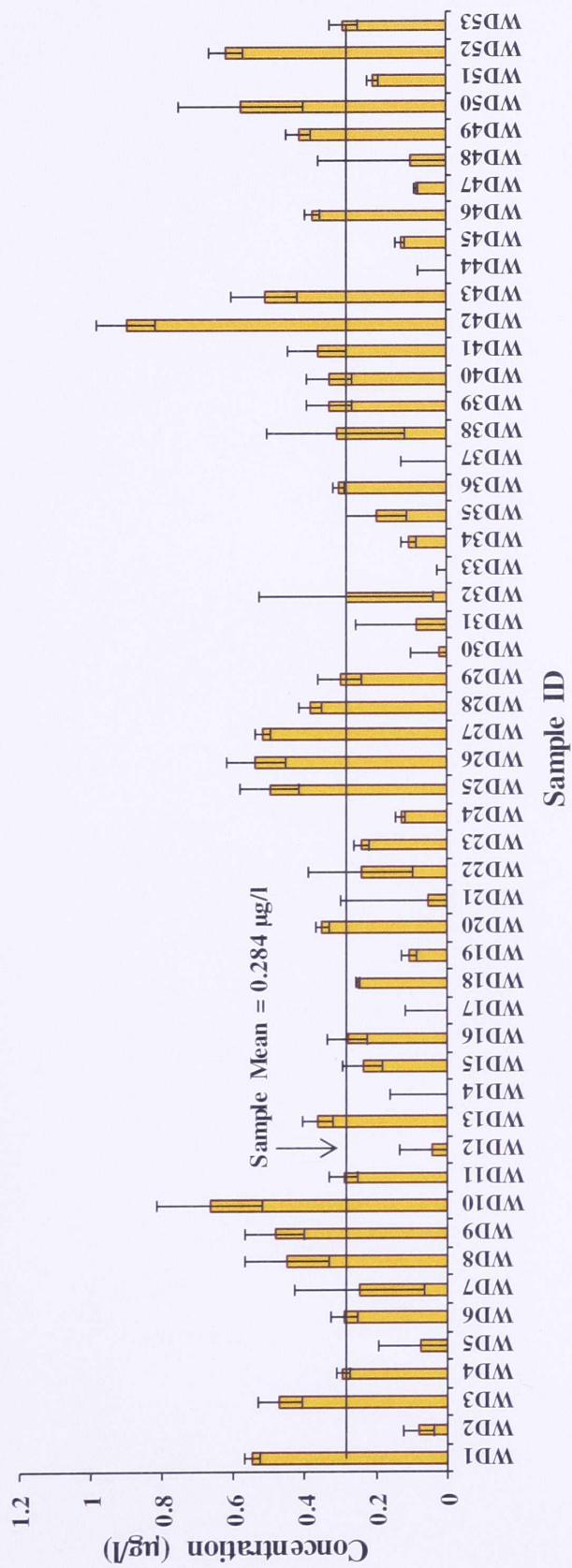


Figure 15c. Concentrations of arsenic in wet deposition

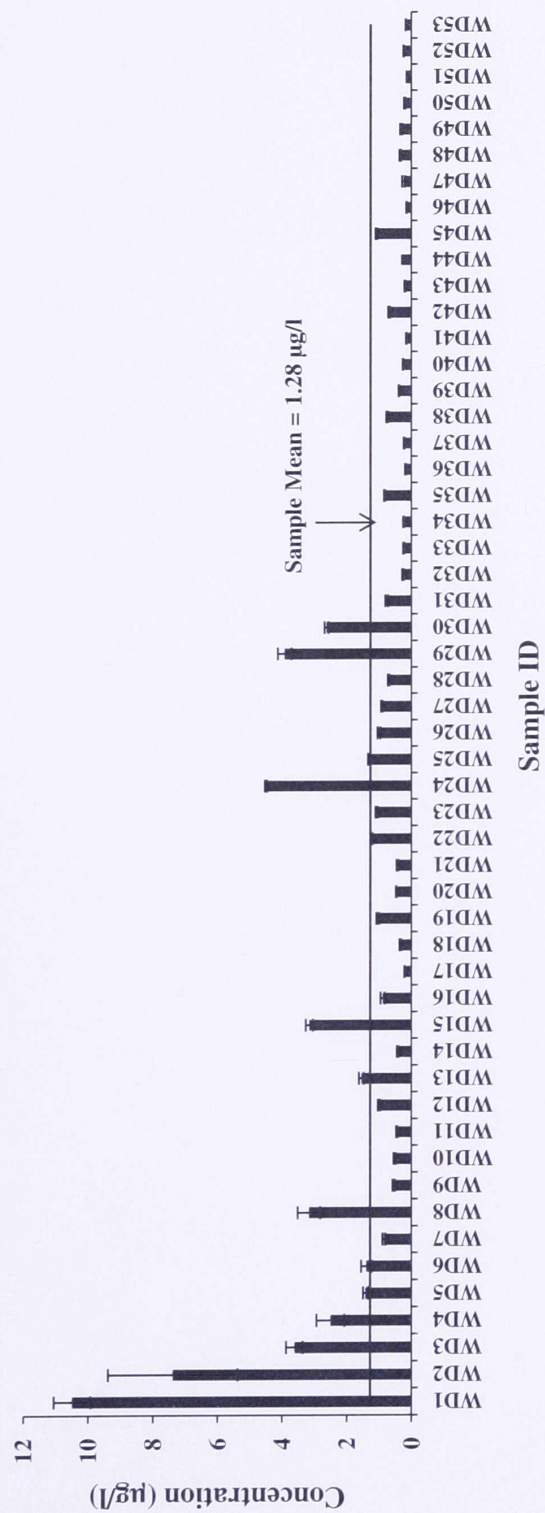


Figure 15d. Concentrations of lead in wet deposition

3.4.2. Monthly variation of heavy metals in wet deposition

One can clearly observe an increase in concentration of Cd from the months of January, 2010 to July, 2010 (Figure 16a). It was also observed that concentrations for Cd declined after the construction of the recreation center at CSU in the month of August, 2010*. For the months of October, 2010 and January, 2011, average concentrations were 0.0152 $\mu\text{g/l}$ and 0.0154 $\mu\text{g/l}$, respectively, which were the lowest concentrations reported for Cd over the 15 month sampling period. The highest concentration for Cd was observed in February, 2011 (0.223 $\mu\text{g/l}$).

In the case of Cr, the highest monthly concentration average of 29.3 $\mu\text{g/l}$ was reported in the month of February, 2010 (Figure 16b). Further investigation revealed that in February and March of 2011, consecutively low concentrations of 0.4901 $\mu\text{g/l}$ and 0.217 $\mu\text{g/l}$, respectively, were observed. Construction of recreation center could be the reason for high levels of Cr during the month of February. However, coal combustion, waste incineration and the metal industry are three other regional sources that may have influenced Cr concentrations in our study (Hlavay *et al.*, 1998).

Arsenic concentrations were highest in the months of July, 2010 (0.416 $\mu\text{g/l}$), January, 2011 (0.385 $\mu\text{g/l}$) and March, 2011 (0.428 $\mu\text{g/l}$) (Figure 16c). An in depth examination enabled the observation of a high-low-high pattern for the months of January, February and March of 2010 and for the same months in 2011. The highest As averages reported in this study seem to agree with concentrations reported by Wang and Mulligan, (2006) in the Canadian region. The increase in concentration reported during the summer month of July may be due to increased use of pesticides on agricultural farmlands. A two year study may perhaps provide more information on the influence on agricultural farming on actual monthly arsenic trends. Landing *et al.* (2010), reported lowest arsenic concentrations in Pensacola, Florida, from November to March. Conko *et al.* (2004) reported the highest arsenic concentrations in the months of July and August in Reston, Virginia.

Pb concentrations showed high month to month variability. This is in agreement with other findings by Zheng *et al.* (2005) in Hong Kong, China. The highest monthly

concentrations for Pb were observed in the month of January, 2010 (5.99 $\mu\text{g/l}$) and the lowest in the month of March, 2011 (0.204 $\mu\text{g/l}$) (Figure 16d). During the first 8 months of sampling, Pb concentrations were generally higher than that of the last 7 months, indicating a decrease towards the end of the construction activity near the sampling site. Another source may be the increase in vehicular traffic on Manchester Expressway during the Christmas and New Year holiday seasons. The highest Pb concentration in January, 2010 could be the result of the synergistic effects of construction and vehicular traffic in January, 2010. In the eastern Mediterranean Sea, higher Pb fluxes were reported from January to April (Theodosi *et al.*, 2010). In this study, maximum monthly concentrations were observed during the months of January to August.

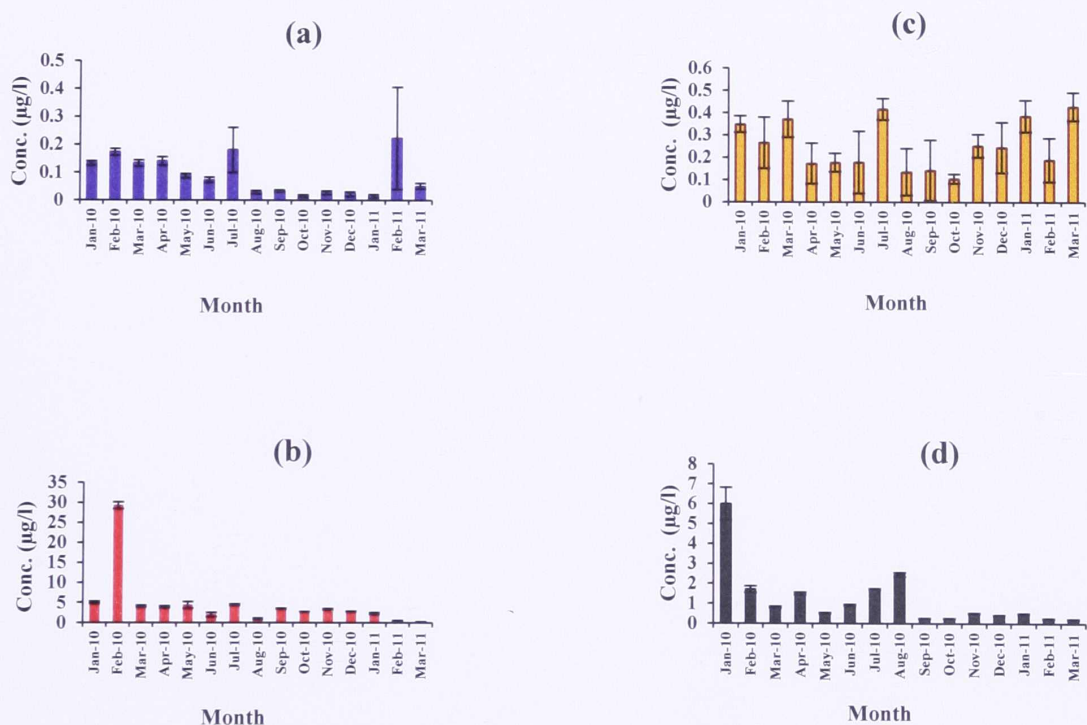


Figure 16. Monthly concentrations ($\mu\text{g/l}$) of a) Cadmium, b) Chromium, c) Arsenic, and d) Lead in wet deposition samples

3.4.3. Seasonal variation of heavy metals in wet deposition

So far, heavy metals in wet deposition samples have been discussed on the basis of trends observed with regard to each individual sample and also monthly averages. Heavy metal concentrations may vary depending on the climatic season. This highest seasonal concentration for Cd ($0.147 \mu\text{g/l}$) was observed in the winter, 2009 (Figure 17a). The highest seasonal concentration level was considerably lower than the maximum Cd seasonal concentration found by Melaku *et al.* (2007) in Washington, DC. The concentrations for Cd decreased from the winter to the spring by 24% and then increased from the spring, 2010 to the summer, 2010 by 7%. The lowest seasonal concentration for Cd was observed in the fall, 2010. The high-low seasonal concentration trends observed for the winter, 2009 to the spring, 2010, and the winter, 2010 to the spring, 2011 may indicate a possible long term pattern (annual trends) and may also suggest the influence of meteorological conditions on local and regional sources.

For chromium, the highest concentration ($13.90 \mu\text{g/l}$) was observed in the winter 2009. A sharp decline (75%) was observed in the concentration of chromium from the winter, 2009 to the spring, 2010 which was comparable to the decrease observed in the winter, 2010 and the spring, 2011. This was in agreement with reports in the Chesapeake Bay area, where Cr concentrations were found to spike towards the late winter and summer (Baker *et al.*, 1994). In support of our findings, higher fluxes for chromium were observed during the warm season in wet deposition in coastal Japan (Sakata and Asakura, 2009). On the contrary, Kanellopoulou *et al.* (2001) found that concentrations were lower during the cold season in Athens, Greece.

Arsenic concentrations displayed a high-low, high-low pattern from the winter, 2009 to spring, 2011 (Figure 17c). Seasonal As concentrations found in this study were lower than those found by Melaku *et al.* (2007) in Washington, DC. It is notable that the winter, 2009 and winter, 2010 had comparable concentrations of $0.354 \mu\text{g/l}$ and $0.359 \mu\text{g/l}$, respectively, reflecting only a 1% increase in concentration between these two seasons. An increase of 73% was observed in the concentration of arsenic from the spring to the summer of 2010, followed by a decrease of 36% in the fall of that same year. In Weston, Virginia, the concentration for As was doubled during the warm season

(May to September) compared to the cold season (November to March) (Conko *et al.*, 2004). On the other hand, in this study, slightly higher concentrations were observed during the cold season as opposed to the warm season which may be due to regional sources.

High seasonal variability was apparent for Pb in wet deposition (Figure 17d). The highest seasonal concentration was observed in the winter, 2009 season and the lowest in the spring, 2011 with values of 2.93 $\mu\text{g/l}$ and 0.167 $\mu\text{g/l}$, respectively. A 91% increase in lead concentrations was observed from the spring, 2010 to the summer 2010 which may be attributed to the use of motor vehicles around the campus (Wedyan *et al.*, 2009; Kanellouplou, 2011).

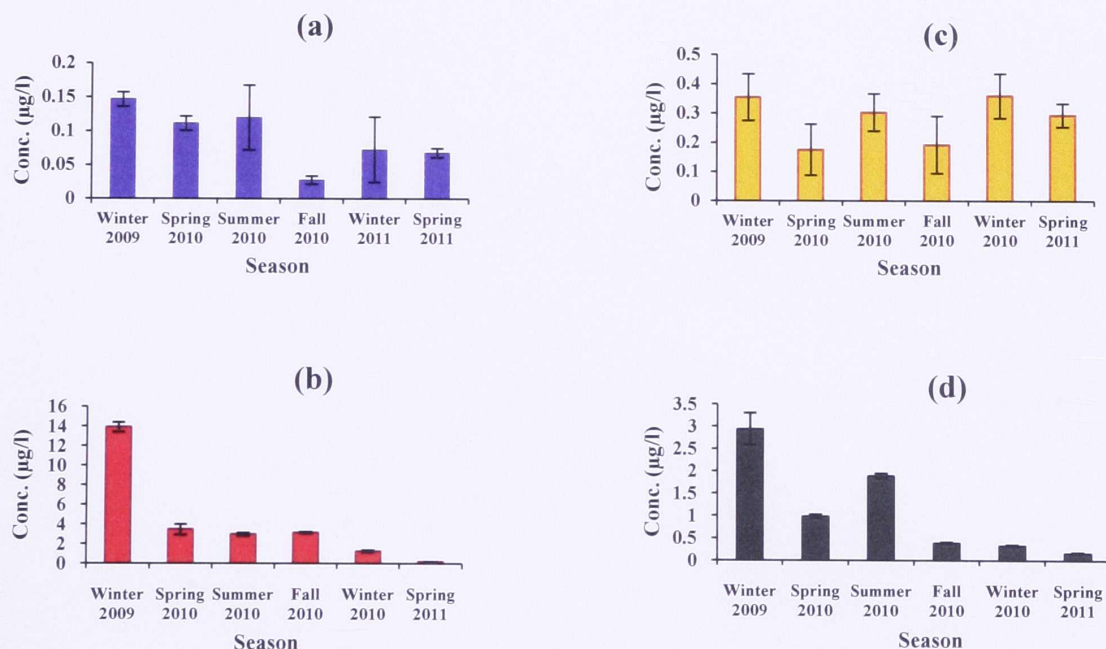


Figure 17. Seasonal variation of a) Cadmium, b) Chromium, c) Arsenic, and d) Lead in wet deposition samples

3.5. Correlation between heavy metals in wet deposition

A weak correlation was observed between lead and chromium with a correlation coefficient of $R^2 = 0.04$ (Figure 18a). In addition, correlation analysis revealed that lead

and cadmium, cadmium and chromium, arsenic and cadmium, arsenic and chromium and arsenic and lead showed a weak correlation with R^2 values of 0.10, 0.11, 0.01, 0.01, 0.04, respectively (Figures 18b-f). The weak correlation between concentrations of these heavy metals indicated that they did not come from a common source (Kanellopoulou *et al.*, 2001).

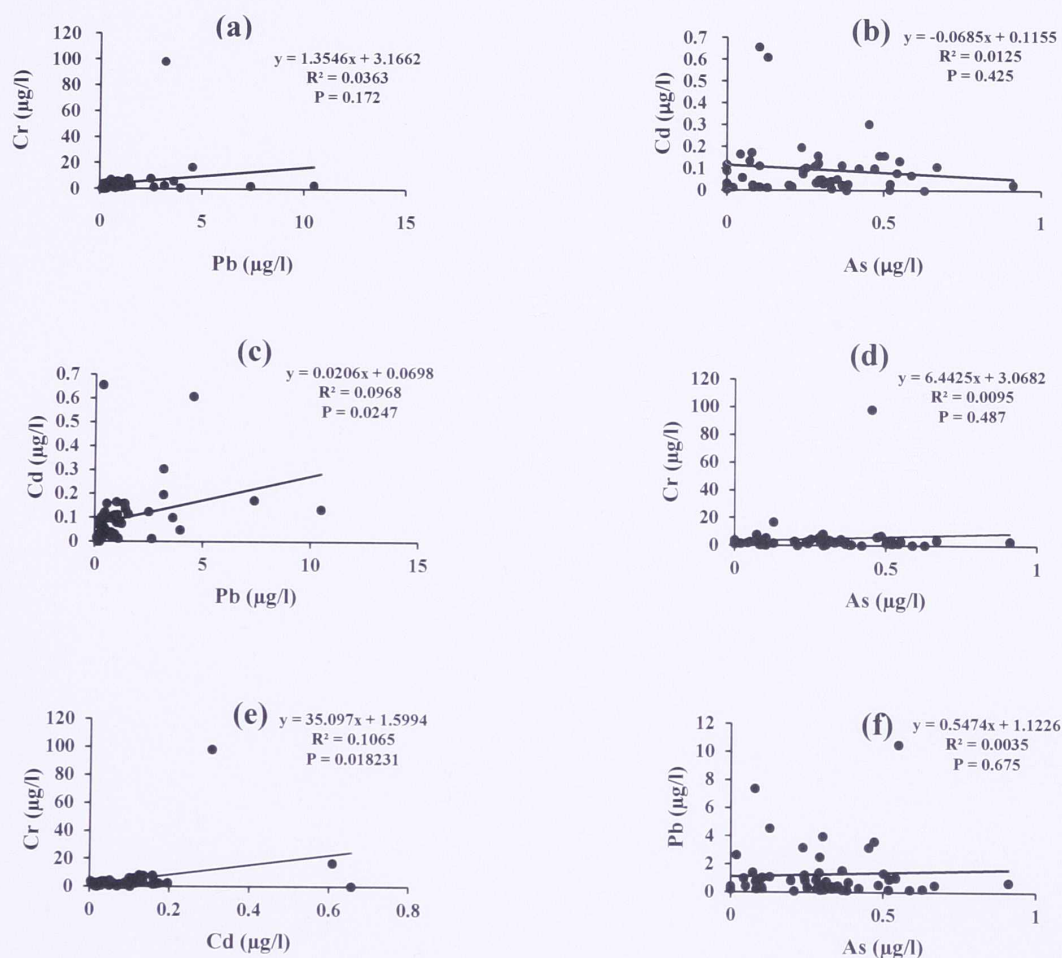


Figure 18. Correlation between heavy metals in wet deposition. a) chromium and lead, b) cadmium and arsenic, c) cadmium and lead, d) cadmium and arsenic, e) chromium and cadmium, and f) lead and arsenic

Results of this study also indicated that there was a statistically significant difference in concentrations between Pb and Cd, and Cd and Cr ($P = 0.025$ and $P = 0.0182$). On the other hand, there was not a statistically significant difference between lead and chromium, arsenic and cadmium, arsenic and chromium, and arsenic and lead. However, a statistically significant difference was found between Pb and Cd, and Cd and Cr, with a

P value of < 0.05 . The lack of a statistically significant difference would mean there was no cause-effect relationship between the two factors (Gotelli and Ellison, 2004).

3.6. Correlation between heavy metals and amount of precipitation

Correlation analyses were conducted in order to see whether there was a relationship between the amount of precipitation and the concentrations of the four heavy metals. Analysis showed that there was not a significant relationship between Pb, Cr, Cd, As and precipitation, with R^2 values of 0.01, 0.02, 0.01 and 0.02, respectively (Figure 19). The results from this analysis were contradictory to the findings by Melaku *et al.* (2007). Melaku *et al.* findings indicated that as precipitation increased the concentration of heavy metals increased. In this study, the observed decrease in concentration may be due to location. Columbus, GA is less urbanized compared to Washington, DC and the surrounding areas, therefore, it is possible that changes with concentration and precipitation may be less obvious.

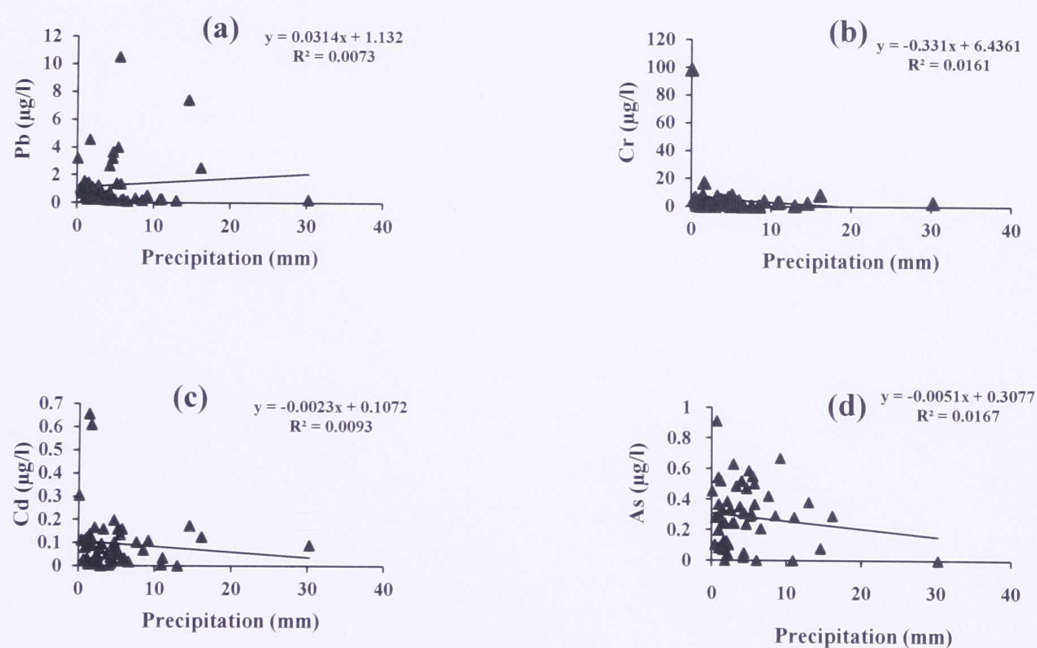


Figure 19. Correlation between precipitation (mm) and heavy metal concentrations for a) lead, b) chromium, c) cadmium, and d) arsenic

3.7. Analysis of ambient air samples

Ambient air results are presented in the same manner as wet deposition. Figure 20 shows the concentrations for Cd, Cr, As and Pb in ambient air collected over the 15 month sampling period. Concentrations of Cd, Cr, As and Pb in ambient air samples ranged from 0.679 - 17.4 ng/m³, ND - 116 ng/m³, ND - 32.8 ng/m³ and 1.78 - 33.3 ng/m³, respectively.

3.7.1. Trends of heavy metals in ambient air

High sample to sample variability was detected for Cd for most of the collection period (DD1-DD48). The highest concentration for Cd, a value of 17.4 ng/m³, was observed in DD24. The mean concentration of Cd (3.72 ng/m³) in ambient air samples was a contradiction to the average Cd concentration reported in ambient air in western Taiwan, a value nearly 7 times smaller (Yang *et al.*, 2003). While a significant amount of Cd in the air is accounted for by windblown dust and volcanic activity on global and regional scales, the influence of the iron and steel industry, waste incinerators, stationary combustion units and the manufacture of fertilizer may also contribute to Cd concentrations on a localized scale (European Commission, 2001). A precision of < 5% was observed for 96% of the samples for Cd in ambient air.

For Cr, one can clearly identify a pattern in ambient air that is different from the pattern observed in wet deposition. For example, for samples DD1 - DD34, concentrations were below the sample mean but subsequently increased (Figure 20b). Generally, concentrations ranged from ND to 116 ng/m³. The highest concentration for Cr in this study was several times higher than the maximum concentration observed in the Gulf of Aqaba, Red Sea and near two dumpsites in Alexandria, Egypt (Rashad *et al.*, 2007; Chen *et al.*, 2008). Approximately 64% of the samples were below 22 ng/m³ (Figure 20b). Results show the distinct influence of Cr sources during the second half of the sampling period. Patterns observed from samples DD40 to DD47 were inconsistent with the rest of the samples and indicate a trend of increasing Cr concentrations throughout that 8 week sampling period. Evidently, concentrations seemed to increase in sequence until DD44 and then decrease again. Such patterns may suggest the influence of mesoscale climatic conditions on atmospheric deposition of air pollutants. However, further

investigation is needed to determine direct relationships. A precision of $< 5\%$ was observed for 76% of samples analyzed for Cr in ambient air.

A clear indication of lower arsenic concentrations in ambient air is evident for the first 34 weeks of sampling (Figure 20c). Arsenic concentrations ranged from ND to 32.80 ng/m^3 . In this study, the average concentration of 22 ng/m^3 was comparable to the average reported by Gidhagen *et al.* (2002) in D.de Almagro, Chile. Clusters of increased arsenic concentrations were observed from DD35 to DD45, DD48 to DD62 and from DD55 to DD60. Evidently, this pattern may indicate common local sources of arsenic which may be agricultural practices in the area. Furthermore, it may also suggest a combined relationship between soil or dust resuspension and changes in climate dynamics.

Concentrations for lead in ambient air ranged from a minimum of 1.78 ng/m^3 to a maximum of 33.30 ng/m^3 (Figure 20d). The sample mean for lead was 8.14 ng/m^3 in ambient air. This average was a magnitude of 2-3 times higher than the average found near a highway in northwestern, New Jersey (Xia and Gao, 2011). High sample to sample variability was observed for lead. In addition, only 38% of samples were above the sample mean. In this study, road dust resuspension from traffic seemed to be a possible source for lead. In addition, the level of concentration variability observed may indicate consistent sources of lead throughout the sampling period and may also suggest that another source rather than construction was the predominant influence on lead concentrations. A precision $< 5\%$ was found for 86% of the samples analyzed for Pb in ambient air.

Particulate matters from roadside soil or dust can extensively influence heavy metal concentrations in the atmosphere. As a result, high concentrations of total heavy metals may be explained by soil resuspension (Azimi *et al.*, 2005). Fine particles from the roads may travel further than 100 m and may be incorporated into coarse particulate matter, hence contributing to background levels of heavy metals (Xiao-li *et al.*, 2006). In addition, coarse particles from motor vehicles in areas with heavy traffic may travel 100 to 150 m away from the source due to gravitational settling (Hitchins *et al.*, 2000; Conko *et al.*, 2004). Due to the fact that the sampling site in this study was located near three

main roads, road side dust resuspension from traffic may be considered a possible source of cadmium, lead and chromium.

The amount of heavy metals in the air at any given period is influenced by wind speed and direction, climate and topography (Onder *et al.*, 2007). As a result, fossil fuel combustion could also be a possible source of arsenic and lead (Baker *et al.*, 1994; Ozaki *et al.*, 2004; Balakrishna *et al.*, 2011).

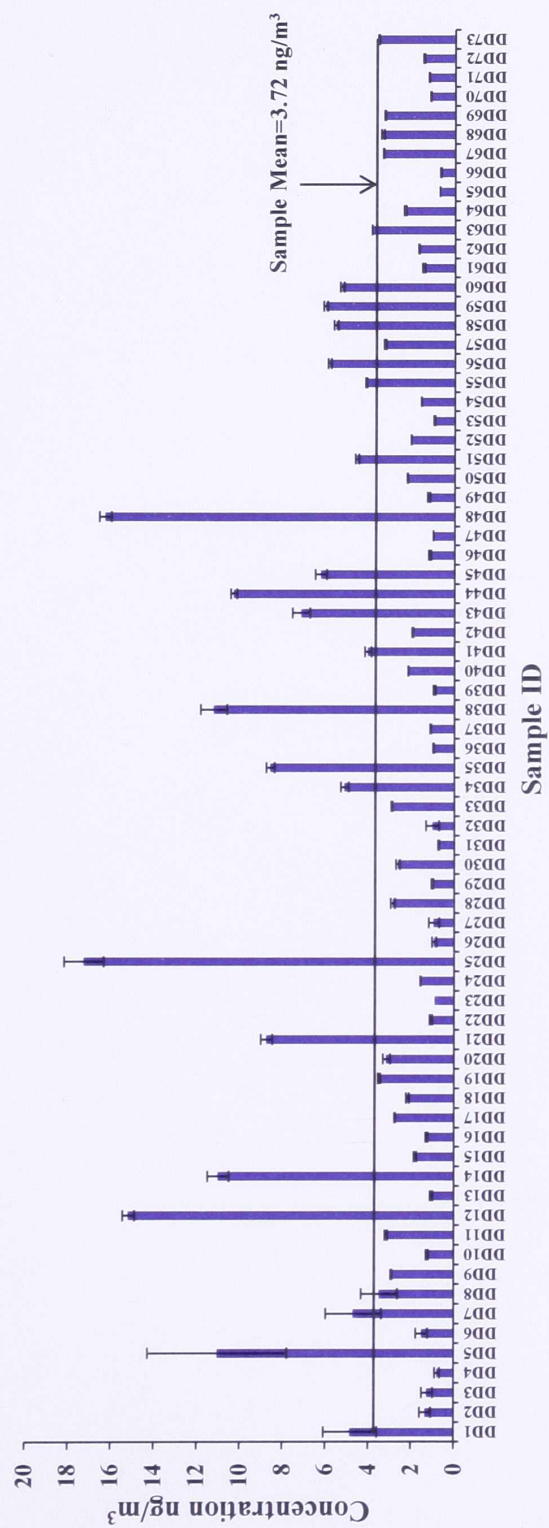


Figure 20a. Concentrations of cadmium in ambient air

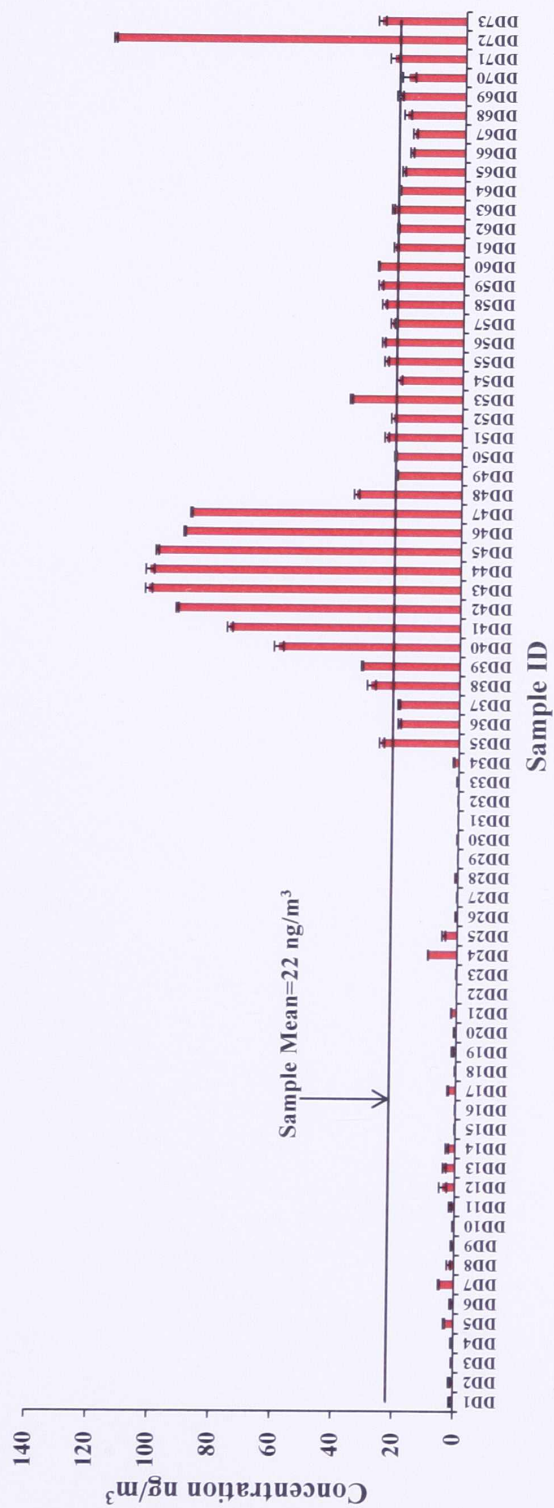


Figure 20b. Concentrations of chromium in ambient air

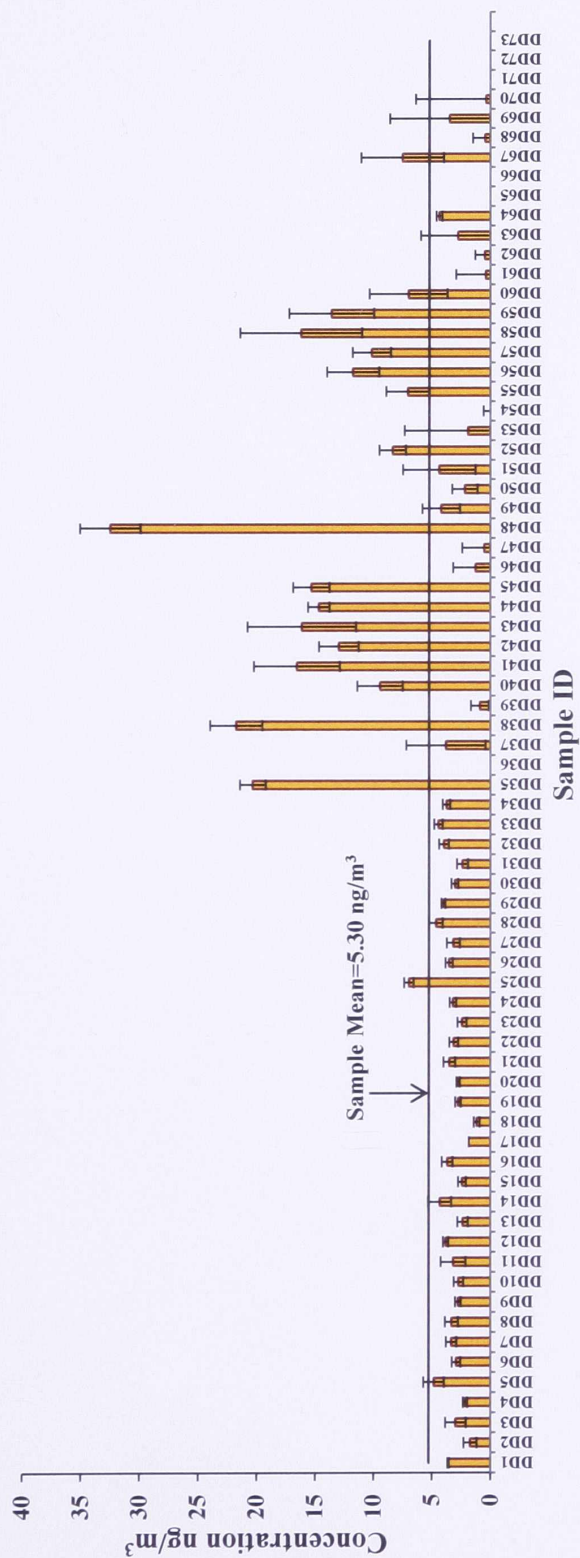


Figure 20c. Concentrations of arsenic in ambient air

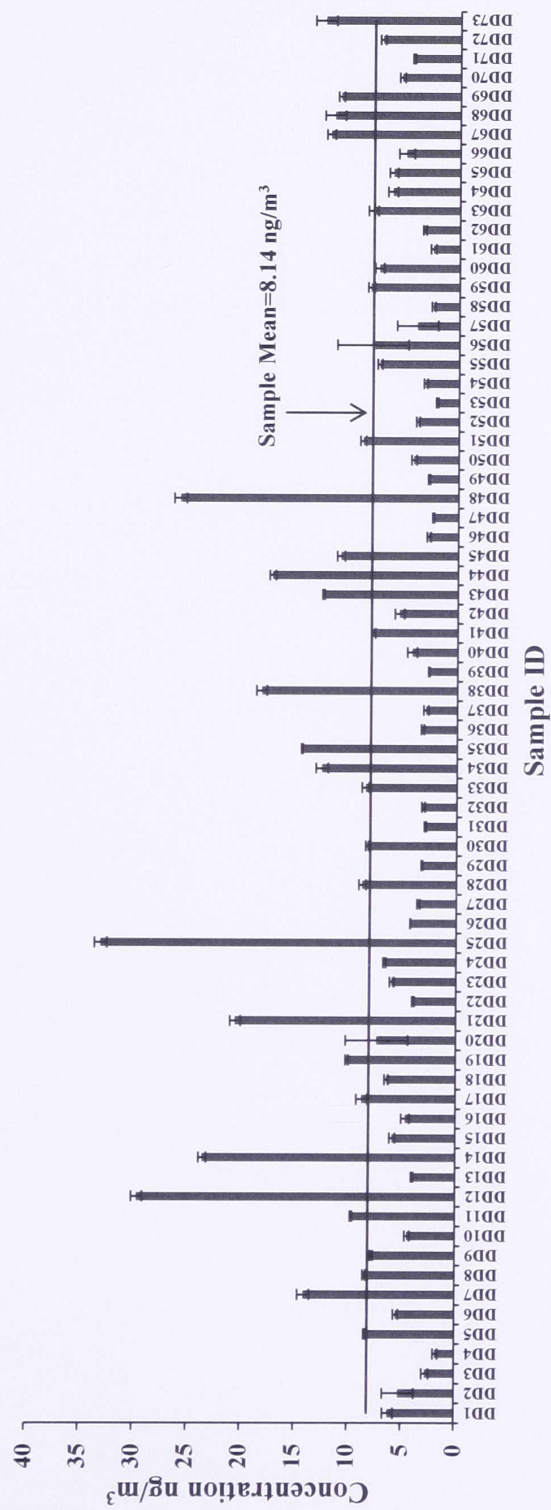


Figure 20d. Concentrations of lead in ambient air

3.7.2. Monthly variation of heavy metals in ambient air

The concentrations for cadmium in ambient air showed high monthly variability. Monthly concentrations for Cd in ambient air ranged from 1.67 ng/m^3 in the month of July, 2010 to 7.07 ng/m^3 in the month of October, 2010 (Figure 21a). In the north-western Mediterranean coast of France, peaks observed during the month of October were explained by changes in the direction of the prevailing winds (Heimbürger *et al.*, 2010). Evidently in this study, construction is a probable local source of Cd in ambient air, although the distinct pattern reported for Cd in wet deposition is different in this case. In addition, motor vehicular traffic from the CSU campus parking lot and roads may account for Cd, Cr and Pb concentrations in ambient air. Chettri (2000) attributed high levels of Cd in Kathmandu, Nepal to tires, galvanized vehicular parts and lubricating oils found in motor vehicles.

For Cr, the months of September and October showed the two highest concentration values of 72.96 ng/m^3 and 83.64 ng/m^3 , respectively. The lowest concentration of 0.13 ng/m^3 was observed in the month of July, 2010. During the first 7 months of sampling lower concentrations were observed compared to the last 8 months. One can clearly see that from August a marked increasing concentration trend is present (Figure 21 b). After the month of July, concentration values increased to monthly values ranging from 19.20 ng/m^3 to 83.64 ng/m^3 . Although concentrations values were higher from November, 2010 to February, 2011 than January, 2010 to July 2011, a marked decline was observed until March 2011. Monthly trends observed for Cr indicate the effect of vehicular traffic on concentration patterns.

Ambient air concentration for arsenic ranged from 0.085 ng/m^3 to 12.98 ng/m^3 during the months of March, 2011 and October 2010, respectively (Figure 20c). Similar to chromium, peak concentrations for arsenic were reported in the months of September, 2010 and October, 2011. Increases in concentrations in the Baltic Coast area were due to burning coal in heating systems (Jarworski, 2006). In this study, this may be a possible source for increased arsenic concentrations during the cold months in addition to general wood burning in the area. The lowest concentration of arsenic was observed in March, 2011. The months of August, 2010, September, 2010 and October, 2011 showed an

increasing trend. The concentration trends observed during the months of August to October may suggest agricultural sources.

Monthly concentration trends for Pb in ambient air were similar to the trends observed for Cr. The highest concentrations were observed from March to October, 2010. This observation was comparable to the results found by Theodosi *et al.* (2010) in the eastern Mediterranean where highest concentrations were observed from May to October. The general trend observed for lead in ambient air suggests that traffic emissions might be the main source for concentration peaks. Brake liners on cars are considered a main source of lead in the air specifically in areas with heavy traffic (Xiao-li *et al.*, 2006; Sezgin *et al.*, 2003).

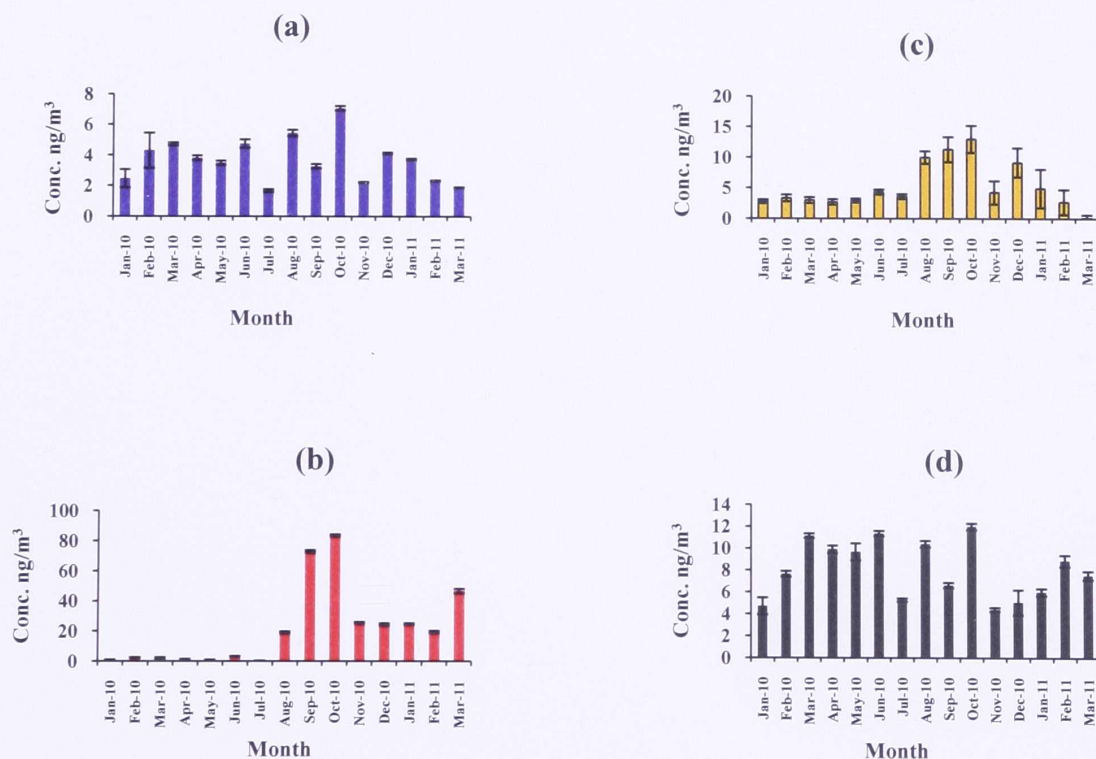


Figure 21. Monthly variation of a) Cadmium, b) Chromium c) Arsenic, and d) Lead in ambient air samples

Moreover, Pb concentrations within the vicinity of a freeway are usually higher than away from its proximity (Sabin *et al.*, 2006). This may be due to the fact that road dust particles from ongoing traffic can be resuspended in the air.

3.7.3. Seasonal variation of heavy metals in ambient air

Aerosol particle emissions are affected by seasonal changes in the spring and summer seasons particularly around major holidays (Hussein *et al.*, 2004). In this study, the highest Cd concentrations in ambient air were observed in the spring, 2010. Seasonal patterns observed for Cd in ambient air suggest fuel combustion from traffic emissions as a probable source of Cd in the atmosphere (Irwin, 1997; Xiao-li *et al.*, 2006). A 44% increase in concentration observed from the summer to the fall may be attributed to the resumption of class sessions and climatic conditions.

Concentration levels for Cr were low during the winter, 2009 but noticeably higher in the winter, 2010, a level slightly higher than that observed during the summer, 2010 (Figure 22a). This observation is in agreement with the findings by Moreno *et al.* (2011) in Barcelona, Spain. For Chromium, the two highest concentrations of 54.40 ng/m³ and 72.22 ng/m³ were observed in the fall of 2010 and the spring of 2011, respectively. Seasonal variability observed for Cr in ambient air samples may be related to factors such as temperature, humidity, vehicular frequency, and wind speed (Sabin *et al.*, 2006).

The highest seasonal concentration of arsenic in ambient air was observed during the fall, 2010 (Figure 22c). This was a contradiction to concentrations in Łódź, Poland where As concentrations were higher during the winter (Krzemińska-Flowers *et al.*, 2006). Moreno *et al.* (2011) also found higher As concentrations in PM_{2.5} and PM₁₀ during the winter. In this study, a 112% increase in arsenic concentration was observed from spring to summer, 2010.

Seasonal concentrations for lead however, were lowest in the winter of 2011 and highest in the spring of 2010 season (Figure 22d). In Los Angeles, Sabin *et al.* (2006) found Pb concentrations to be highest in the fall. In this study, Pb concentrations for both the spring of 2010 and the spring of 2011 were the two highest concentrations throughout all seasons indicating the influence of traffic emissions on Pb concentrations in ambient air.

Increases from the winter, 2009 to the spring, 2010 and the winter, 2010 to the spring, 2011 were 73% and 51%, respectively. Furthermore, concentrations of Pb decreased by 39% from the spring to summer, 2010 and subsequently increased during the fall. The latter observation was consistent with observations made by Marcazzan *et al.* (2001) in Milan, Italy for Pb in PM_{2.5}. Similarly, decreases in Pb concentrations were observed during the summer in Paris, France by Azimi *et al.* (2005). In this study, the decrease observed during the summer may be due to a decline in traffic during that season (Gélinas *et al.*, 2000). In Seoul, Korea, maximum Pb concentrations observed in the spring season were due to soil resuspension and in the winter biomass burning (Heo *et al.*, 2009). These sources may provide a possible explanation for lead concentrations in this study.

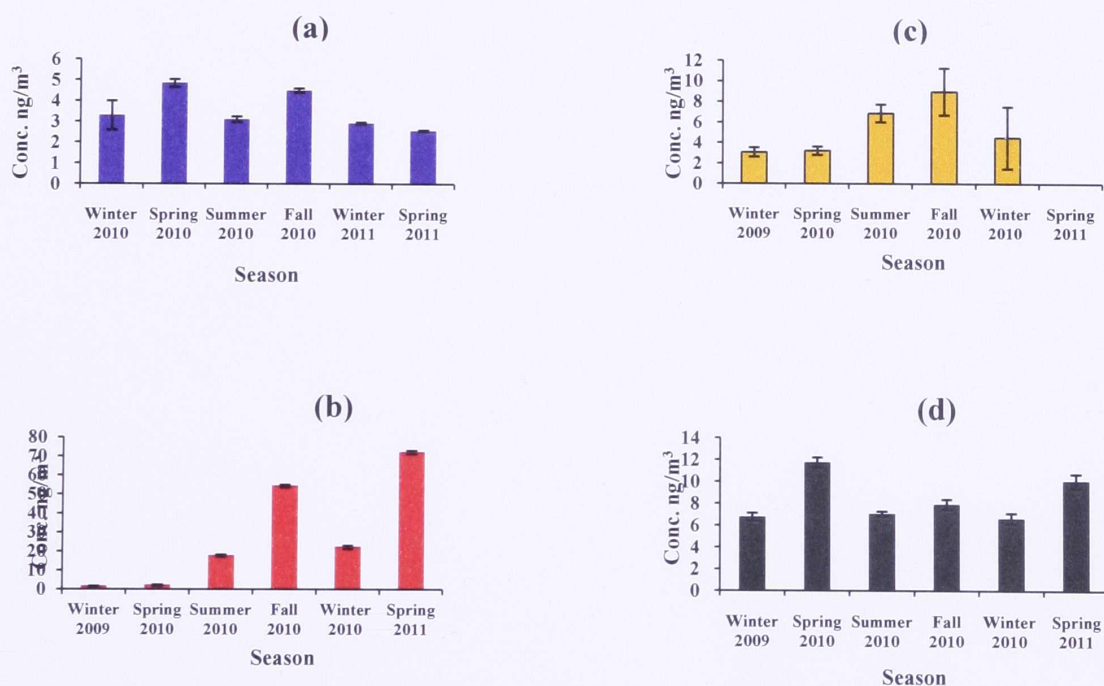


Figure 22. Seasonal averages for concentrations of Cadmium, Chromium, Arsenic, and Lead in ambient air samples

3.8. Correlation between heavy metals in ambient air

In this study, weak correlations were observed between lead and chromium, cadmium and chromium, arsenic and chromium, arsenic and cadmium, and arsenic and lead with correlation coefficients of 1×10^{-5} , 0.0069, 0.134, 0.369 and 0.169, respectively. On the other hand, when investigated, lead and cadmium exhibit an identical pattern of variability. Monthly and seasonal concentration trends for cadmium and lead in ambient air reveal that these two heavy metals have similar patterns.

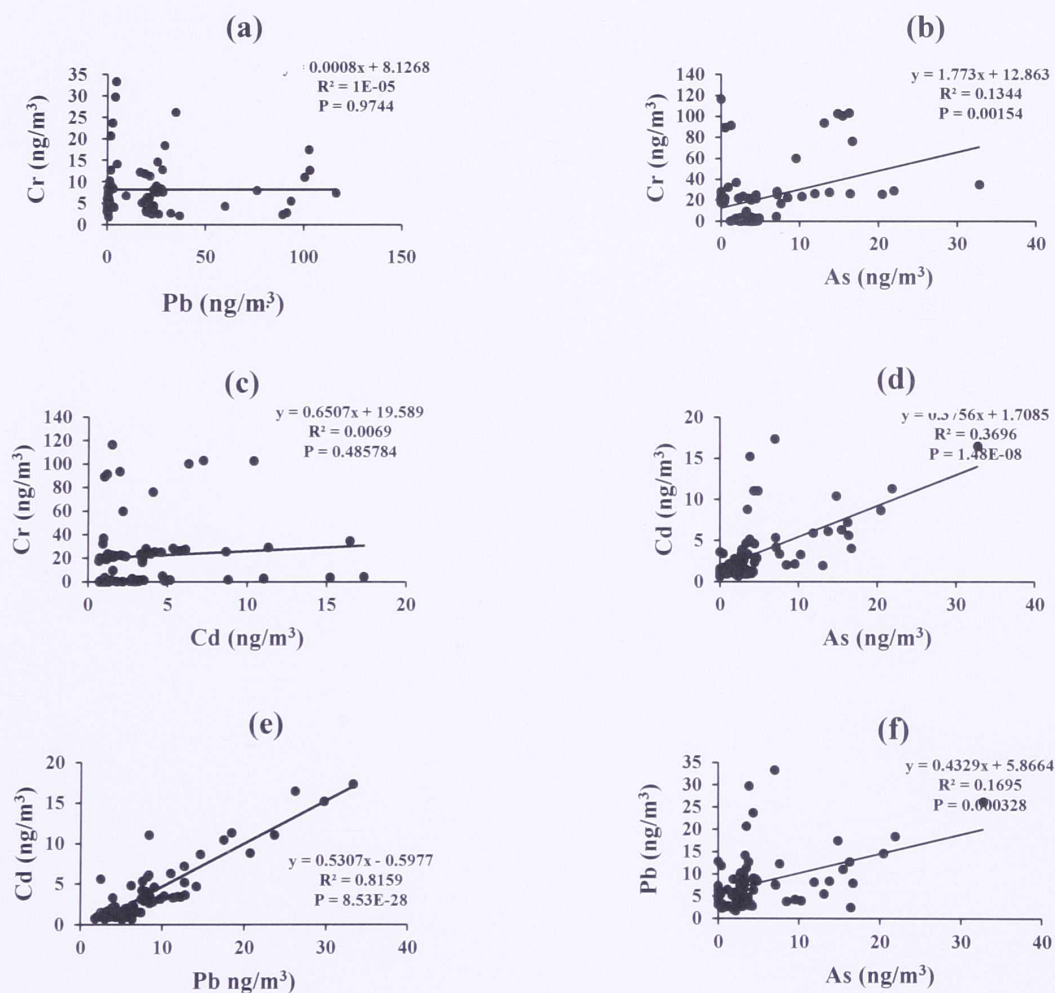


Figure 23. Correlation between heavy metals in ambient air. a) chromium and lead, b) cadmium and chromium, c) cadmium and lead, d) cadmium and arsenic, e) chromium and arsenic, and f) lead and arsenic

For example, from January to October similar increasing and decreasing concentration are observed. One can observe a strong correlation between lead and cadmium with an R^2 value of 0.816 (Figure 23c). This is in agreement with reports by Momani *et al.* (2000) in Amman, Jordan. They attributed a strong correlation found between lead and cadmium to motor vehicular emissions.

3.9. Comparison between heavy metals in wet deposition and ambient air

Pearson's correlation between individual heavy metals in wet and dry deposition showed that there was a negative correlation between all metals (Table 10). These results were contrary to those found by Melaku *et al.* (2007) in Washington, DC. A similar correlation analysis conducted by Farahmandkia *et al.* (2010) in Zanjan, Iran showed positive correlations for Cd, Cr and Pb concentrations in wet deposition and ambient air.

For all the heavy metals, concentrations observed in wet deposition were generally inconsistent with those obtained in dry deposition. For instance, unlike wet deposition, arsenic concentrations in ambient air were lower during the winter of 2009 and the spring 2010. A 112% increase was observed from the spring to the summer for arsenic in wet deposition whereas in ambient air a 73% increase was observed during the same period. For lead in ambient air, increases from the winter, 2009 to the spring, 2010 and the winter, 2010 to the spring, 2011 were 73% and 51%, respectively. For lead in wet deposition however, decreases rather than increases were observed in concentrations during the same periods.

Table 10. Pearson correlation of heavy metals in wet deposition and ambient air (dry deposition)

	Dry	Cd	Cr	As	Pb
Wet	-	-	-	-	-
Cd	-	-0.0488	-	-	-
Cr	-	0.0952	-0.206	-	-
As	-	-0.569	-0.320	-0.125	-
Pb	-	-0.129	-0.4304	-0.278	-0.179

Conclusion

Hazardous air pollutants such as toxic heavy metals are significant in air quality studies in the United States and various parts of the world. The more we know about them, the better we are able to understand and minimize the occurrence of toxic metals like lead (Pb), cadmium (Cd), arsenic (As) and chromium (Cr), which can essentially attack specific areas in the human body and cause damage. In this study, individual concentration trends, monthly variation, seasonal variation, the relationship between heavy metals and precipitation, and the relationship between heavy metals in wet deposition were simultaneously investigated. In addition, heavy metal concentrations in wet deposition were compared to heavy metal concentrations in ambient air in Columbus, Georgia. Samples were collected from wet deposition and ambient air, using a TPC 3000 and multistage cyclone impactor, respectively. All samples were analyzed using GF-AAS to quantify concentrations of the four toxic heavy metals.

All heavy metals concentrations were within acceptable limits set by OSHA and WHO. The highest concentration for cadmium in wet deposition samples was 0.656 µg/l, for chromium 98.2 µg/l, for arsenic 0.90 µg/l and for lead 10.50 µg/l. Heavy metal concentrations in wet deposition showed the following trend, Cr > Pb > As > Cd. Monthly concentrations were highest for cadmium in the month of February, 2011 with an average concentration level of 0.223 µg/l. For chromium an average concentration of 29.3 µg/l was observed in the month of February, 2010. Monthly averages of 5.99 µg/l for lead and 0.428 µg/l for arsenic were observed in the months of January, 2010, and March, 2011, respectively. Furthermore, in wet deposition samples, results indicated that Cd, Cr, As and Pb concentrations were higher during the winter 2009 season when construction was ongoing near the sampling site.

Correlation analysis of wet deposition samples showed that there was a weak correlation between all heavy metals indicated by an $R^2 \leq 0.1$. The same analysis between precipitation and concentration of heavy metals in wet deposition also indicated a weak correlation for all heavy metals.

For ambient air samples, the highest concentration for cadmium was 17.4 ng/m^3 , chromium 116 ng/m^3 , arsenic 32.80 ng/m^3 and lead 33.30 ng/m^3 . Heavy metal concentrations in ambient air showed the following trend, $\text{Cr} > \text{Pb} > \text{As} > \text{Cd}$. Monthly averages for cadmium were highest in the month of October (7.07 ng/m^3). An average of 83.64 ng/m^3 was observed in the month of October for chromium and 12.98 ng/m^3 was observed in the same month for arsenic. Similarly for lead, the highest monthly concentration (11.96 ng/m^3) was observed in the month of October. Whilst the highest seasonal Cd concentration in ambient air was observed in the spring, 2010, highest concentrations for chromium were also observed in the spring, 2011. In addition, for arsenic, the highest seasonal concentration was observed during the fall, 2010 and highest seasonal concentration for lead was observed in the spring, 2010 season (11.74 ng/m^3). However, general seasonal ambient air trends indicated that during the fall semester when students returned back to school, concentrations of Cd, Cr, As and Pb were comparatively higher.

A clear determination of the actual heavy metal pollution sources was beyond the scope of this study. However, the main implications for probable sources of heavy metals in ambient air and wet deposition in this study are traffic emissions which may include road dust resuspension and construction. For arsenic, results implied a connection between concentration and wood burning for heating during the cold season.

There was a statistically significant difference between concentrations of heavy metals in wet and dry deposition samples. In addition, heavy metals like arsenic showed a possible monthly pattern in wet deposition over 15 months of sampling. A weak correlation was observed between heavy metals in ambient air, except for lead and cadmium, which may indicate a connection with a common source such as vehicular traffic.

Overall seasonal variability observed in both wet deposition and ambient air samples also suggested traffic and construction sources for Cd, Cr, As and Pb.

Future Work

Continuous sampling to see whether annual patterns will develop is highly recommended. A future study to collect data for more than one year may be necessary to observe annual patterns. For example, in this study, distinct monthly peaks in concentration were observed for arsenic in January, February and March in wet deposition samples. In addition, after construction, concentrations of heavy metals were clearly returning to background levels. As a result, a longer study may reveal possible sources.

Tests on several locations around the Columbus area are also highly recommended. Conko *et al.* (2004) found that similarities in concentrations from different locations could indicate a common source. A future analysis of the impact of wind speed and direction could be a necessary component in determining the sources of heavy metals within this study.

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